GEORGIA INSTITUTE OF TECHNOLOGY
STATE ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

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QUARTERLY REPORTS NO. 1-3

FINAL REPORT

and

SPECIAL REPORT NO. 1

PROJECT NO. 161-101

INVESTIGATION OF AGGREGATION OF FINE PARTICLE MATTER SUSPENDED IN AIR

BY

J. M. DALLAVALLE,
CLYDE ORR, JR., AND L. A. WOODWARD

CONTRACT NO. DA-18-064-CML-402

CHEMICAL CORPS - CAMP DETRICK

FREDERICK, MARYLAND

SEPT. 14, 1950-JUNE 14, 1951

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
Atlanta, Georgia

QUARTERLY REPORT NO. 1

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SEPTEMBER 14, 1950

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This Report Contains 4 Pages

I. SUMMARY

The following pieces of equipment for investigating the aggregation of fine particle matter suspended in air have been assembled or are nearing completion: (1) a La Mer aerosol generator, (2) a DallaValle elutriator adapted as an aerosol generator, (3) a thermal precipitator for aerosol sampling, (4) a metal evaporation chamber for producing a silica film substrate and for shadowing aerosol samples, and (5) a plastic (polystyrene) chamber to contain the aerosol. The first phase of the investigation is confined to a study of the aggregation of dilute aerosols with time.

II. INTRODUCTION

This investigation has as its general objective the study of (1) the effect of concentration and electrical nature of fine particulate matter suspended in air on the rate of aggregation of the individual particles, and (2) the nature of other cohesive factors affecting aggregation in an aerosol.

Despite the vast amount of work which has been done on aerosols, comparatively little is known about their properties. Foremost among the experimental difficulties in any aerosol investigation are the problems of obtaining representative samples for detailed analysis and the lack of reproducibility of particle size and size distribution. Since sampling and production of uniform aerosols are considered of primary importance in the study here reported, several pieces of equipment have been obtained or are being built which will minimize the number of experimental variables. In particular, it is planned to use a monodisperse system of aerosols so that the variable of particle size can be rigidly controlled and to sample with a thermal precipitator which will cause a minimum disturb-

ance of the sample collected. Hence, the variables which affect the aggregation of aerosols should be determined with greater certainty and accuracy than has heretofore been possible.

III. EQUIPMENT

A La Mer monodisperse aerosol generator[1] with auxiliary air filtering and drying equipment has been set up and is now operating satisfactorily. An elutriator described by DallaValle[2] has been fitted with a slow speed stirrer, as shown in Figure 1, so that a solid material of very small and uniform size may be dispersed as an aerosol. Samples of powdered silica and bacteria (sterile) of a very uniform size have been obtained. A thermal precipitator is nearing completion, constructed from plans furnished by Dr. Carlton E. Brown of the U. S. Army Chemical Corps. A metal evaporation chamber is being adapted for use on this project. It will be employed to produce silica film substrates upon which aerosol samples collected in the thermal precipitator may be preserved for examination, without further treatment, with the electron microscope. This apparatus will also produce low angle shadowing by gold or chromium to obtain dimensional effects of aggregates when that phase of the investigation is reached. A chamber of polystyrene plastic from which aerosol samples may be collected will be built.

IV. FUTURE PROGRAM

As indicated above, production and sampling of aerosols will be thoroughly studied before the influence of the many variables affecting

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(1) Sinclair, D., and La Mer, V. K., "Light Scattering As a Measure of Particle Size in Aerosols. The Production of Monodisperse Aerosols." Chem. Revs. 44, 245 (1949).
(2) DallaValle, J. M., Micromeritics. Pitman Publishing Co., New York, 1948, p. 87.

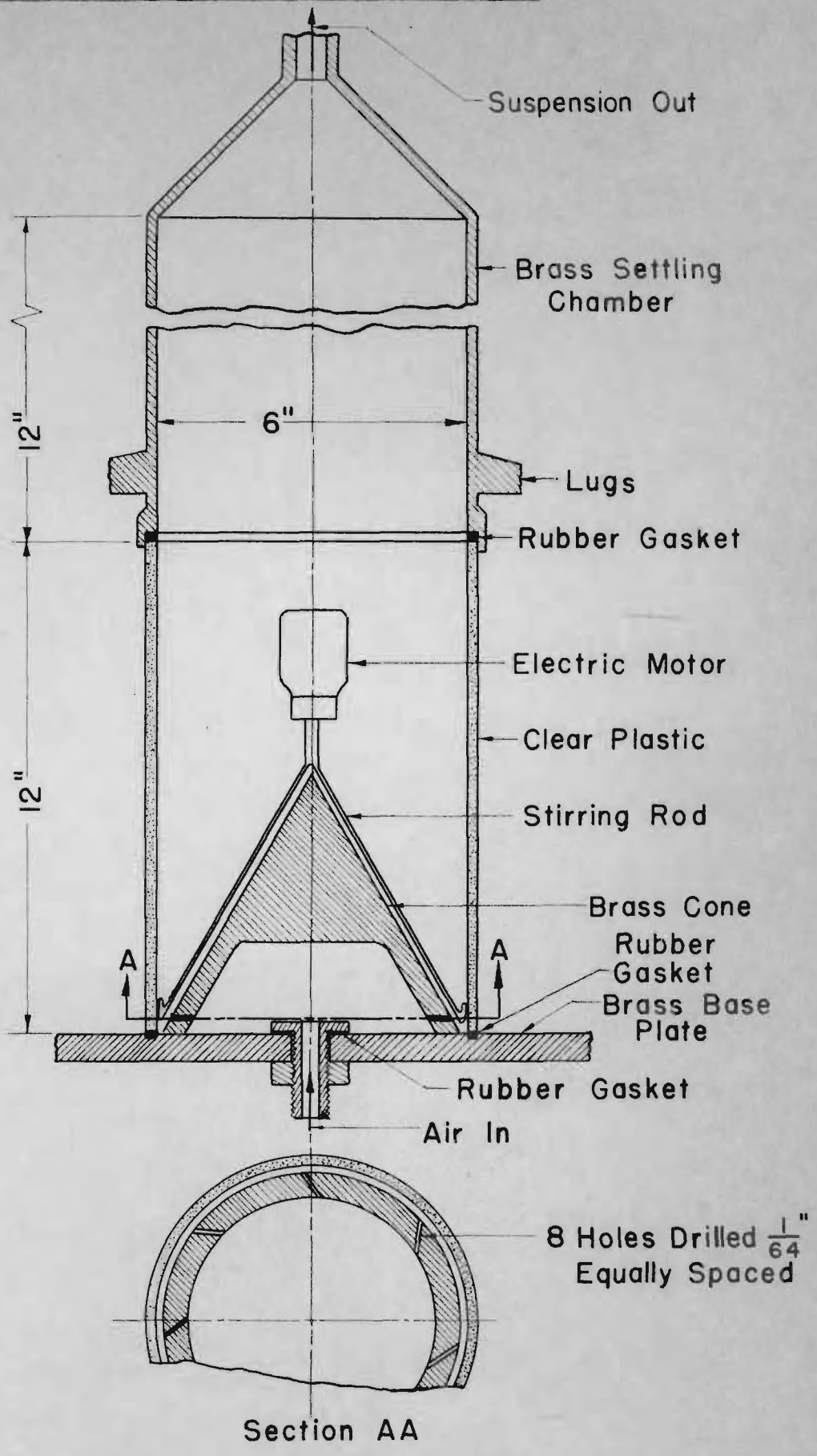

Figure 1. Cross Sectional Drawing Showing Essential Features of the Air Elutriator.

aggregation are considered. An investigation of the aggregation of selected aerosols with time by the use of photomicrographs of thermally precipitated samples is planned. Means of charging and then measuring the charge on aerosols are being considered and equipment for accomplishing this is in the design stage.

Respectfully submitted:

J. M. DallaValle,
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Clyde Orr, Jr.,
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L. A. Woodward,
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Gerald A. Rosselot, Director
State Engineering Experiment Station

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STATE ENGINEERING EXPERIMENT STATION
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QUARTERLY REPORT NO. 2

PROJECT NO. 161-101

INVESTIGATION OF AGGREGATION OF FINE PARTICLE MATTER SUSPENDED IN AIR

By

J. M. DALLAVALLE,
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CONTRACT NO. DA-18-064-CML-402

CHEMICAL CORPS - CAMP DETRICH

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QUARTERLY REPORT NO. 2

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DECEMBER 14, 1950

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This Report Contains 22 Pages

I. SUMMARY

Considerable time and effort have been devoted to an investigation of methods for producing an aerosol of characteristics suitable for studies of aggregation. Ammonium chloride smoke produced with a La Mer generator appears to meet the requirements. The particles are relatively uniform in size, they are easily collected with a thermal precipitator, and few agglomerated particles are ever found. A study of the effects of concentration, size, and electrical charge is planned.

A special report concerning the mathematical analysis of two types of bimodal size distributions often encountered in aerosol studies is being prepared.

II. INTRODUCTION

The general objectives of this project are: (1) the study of the effects of concentration and electrical charge on the rate of aggregation of fine particulate matter suspended in air, and (2) the nature of other factors affecting aggregation in an aerosol.

The experimental work to date has been concerned primarily with establishing techniques and procedures by which a sufficiently monodisperse aerosol can be generated, can be easily collected, and can be examined with the electron microscope.

A mathematical analysis of two types of bimodal particle size distributions found in the case of one investigated aerosol system has been completed and will be the subject of a special report now in preparation.

III. EXPERIMENTAL WORK

The production of alumina, silica, stearic acid, and ammonium chloride aerosols has been investigated.

The apparatus for producing the alumina and silica aerosols is shown in Figure 1 of the appendix. Air from a carefully regulated pressure source flows through the flow meter and enters the elutriator tangentially through the base. As the air flows upward through the elutriator it carries with it solid particles of less than a predetermined size. This size is determined by means of Stokes' law. A special alumina (Al_2O_3)[1] having a mean particle diameter of about two microns, and silica[2] having a somewhat smaller mean diameter were used. It was impossible to produce an aerosol with either of these materials without obtaining extensive agglomeration of the individual particles. An electron photomicrograph of a thermally precipitated particle of alumina, Figure 2, shows the magnitude of the effect. Figures 3 and 4 show the thermal precipitator in location in the aerosol chamber, and, incidentally, show the flow characteristics of an aerosol stream at a very low rate of flow and in very stable surroundings. Figure 5 is an electron photomicrograph of a particle of alumina which passed through an electric spark discharge and was then thermally precipitated. Increased agglomeration is evident by comparison with the particle shown in Figure 2.

Figure 6 shows the La Mer generator[3] and the aerosol chamber. The production of approximately monodisperse aerosols of stearic acid (the degree of dispersion and the particle size were indicated by the intensity and brilliance of the colors from scattered light) was accomplished after considerable experimentation with air flow rates and generator temperatures. Difficulties were encountered in the collection and electron microscopic

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(1) Produced by the Linde Air Products Co. of New York, N. Y.
(2) Produced by the Tennessee Corporation Research Laboratories of Atlanta, Ga.
(3) Sinclair, D. and La Mer, V. K., "Light Scattering As a Measure of Particle Size in Aerosols. The Production of Monodisperse Aerosols." Chem. Revs. 44, 245-67 (1949).

examination of the aerosol, however. Either no sample would be collected or the sample would be melted by the collection process. Occasionally, the necessary conditions, i.e., heated element temperature, flow rate past the element, and element distance from the surface on which the aerosol was to be collected, would be satisfied and a sample as shown in Figures 7 and 8, would be collected with little or no melting. Figure 9 shows a case in which melting occurred; the heated element in the thermal precipitator was found to be at a temperature of only 41° C. The melting point of stearic acid is 69.4° C. The only explanation that can be offered at present is that the very small spheres have a softening point lower than the melting point of stearic acid in bulk. There are indications that the small spheres are in a metastable state.[4] Sinclair[5] has reported that stearic acid originally deposited as spheres was found to have changed shape by the following day.

Collection by filtration was attempted, but a suitable filter medium was not found. Figure 10 shows one particle collected on lens tissue.

Slow evaporation of the stearic acid spheres was found to occur during the exposure of a sample to the high vacuum conditions existing in the electron microscope. This was of no great consequence in the time necessary to obtain a picture.

In view of these difficulties an aerosol of ammonium chloride was investigated and appears to be admirably suited to the purpose. The first attempts to produce an ammonium chloride aerosol employed the direct mixing of ammonia and hydrochloric acid vapors, but the corrosion caused by a slight excess of ammonia, and the difficulties of producing nuclei and

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(4) La Mer, V. K., "The Preparation, Collection, and Measurement of Aerosols." Proceedings of the First National Air Pollution Symposium, Stanford Research Institute, (1950).

(5) Sinclair, D., "Measurement of Particle Size and Size Distribution." Chapter 8, Handbook on Aerosols, Atomic Energy Commission, Washington, D. C., 1950, p. 100.

controlling the mixing, dictated another method. Also, the aerosol generated by this method, shown in Figure 11, was not monodisperse or of a single crystalline structure. Subsequently it was found that solid ammonium chloride used as stearic acid was used in the La Mer generator gives a satisfactory aerosol. No difficulties are encountered in the thermal precipitation of a sample, since a sufficiently high temperature can be employed in the precipitator without melting or decomposing the sample. The particles can be examined readily in the electron microscope. Few agglomerated particles are produced. Ammonium chloride exhibits an additional property: if an electron photomicrograph is taken without undue delay, the ammonium chloride particles appear as black solids, but, after a few minutes exposure to the electron beam, the particles become rather transparent. Figures 12 and 13 reveal the difference made by a few minutes exposure to the electron beam. It will be noted that no change in the size or shape of the particles is detectable. Intense electron beams sometimes do produce particle size changes.[6] This is actually an advantageous property since some of the same desired information may be obtained without shadowing. Figures 14 and 15, which are of ammonium chloride particles produced by the vapor-mixing process, show this quite distinctly.

IV. NEW EQUIPMENT

The shadowing apparatus shown in Figure 16 is nearly completed. Only portions of the mechanism for manipulating the sample in the shadowing chamber are yet to be made.

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(6) Watson, H. L. and Preuss, L. E., "Motion Picture Studies of Electron Bombardment of Colloidal Crystals." J. Applied Physics 21, 904-7 (1950).

Modifications of the thermal precipitator (see Quarterly Report No. 1 under Equipment) have been made so that from one to five electron microscope screens can be placed in the precipitator at one time, and aerosol samples can be taken at any desired intervals thereafter without disturbing the aerosol. A film made from a two per cent solution of parlodion in butyl acetate and formed on the electron microscope screens before they are placed in the precipitator has proved satisfactory for collecting the aerosol sample. No further preparation of the sample is necessary for microscopic examination or for shadowing with this procedure.

V. RESULTS

The principal result of the experimental work to date is that a material for producing a suitable aerosol has been found and the techniques for handling it have been developed.

A mathematical analysis of two types of particle size distributions encountered in aerosol and other work has been studied. A special report on the subject is in preparation.

VI. FUTURE PROGRAM

The work of the future will be directed toward: (1) obtaining a more monodisperse aerosol of ammonium chloride or investigating other substances that appear to be better suited if such can be found, (2) determining the rate of aggregation of an ammonium chloride aerosol with time, particle size, and concentration, and (3) producing an electrical charge on the particles of the aerosol and determining the effects of such a charge.

Respectfully submitted:

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L. A. Woodward,
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State Engineering Experiment Station

VII. APPENDIX

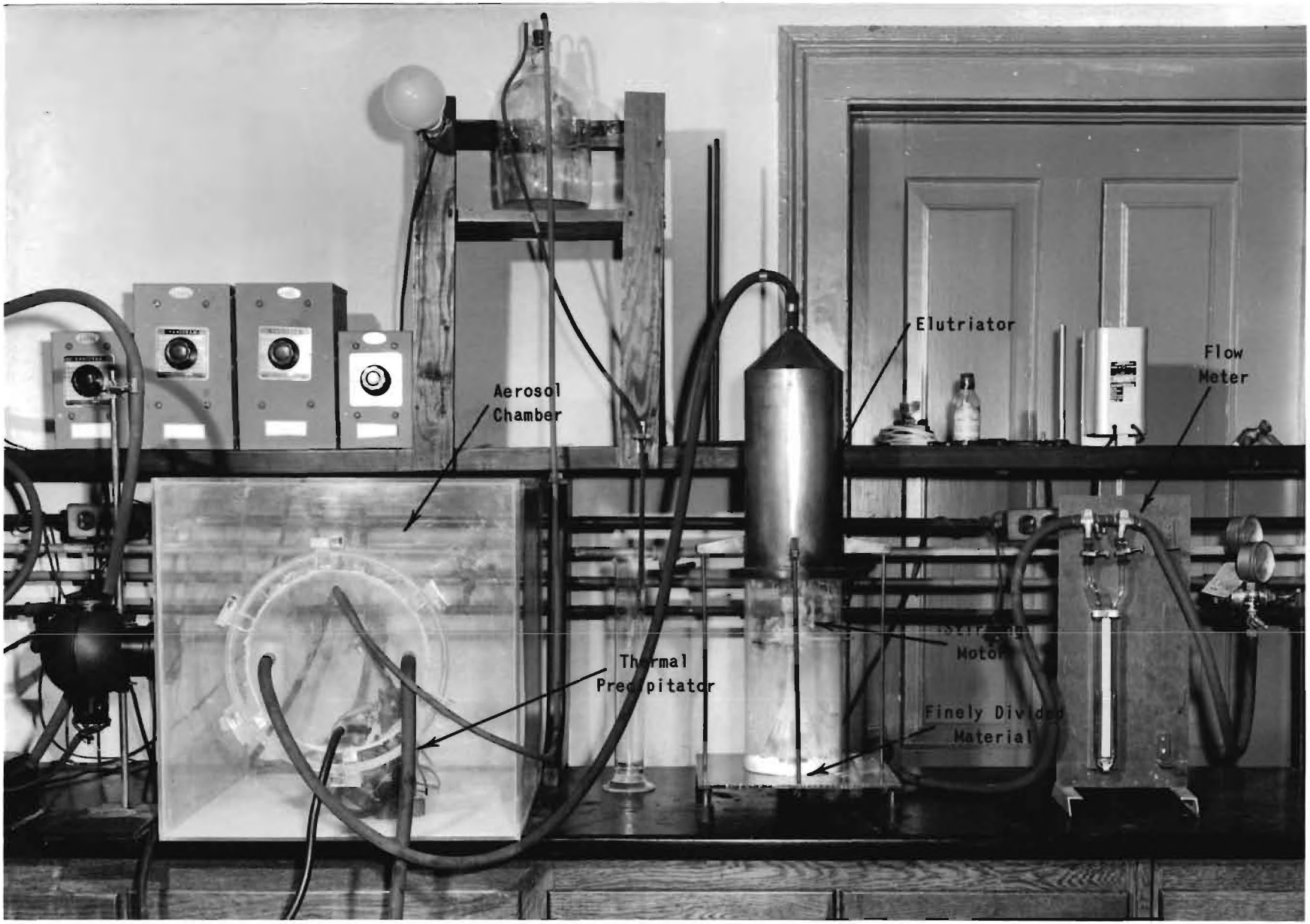

Figure 1. Elutriator Arrangement for the Generation of Aerosols.

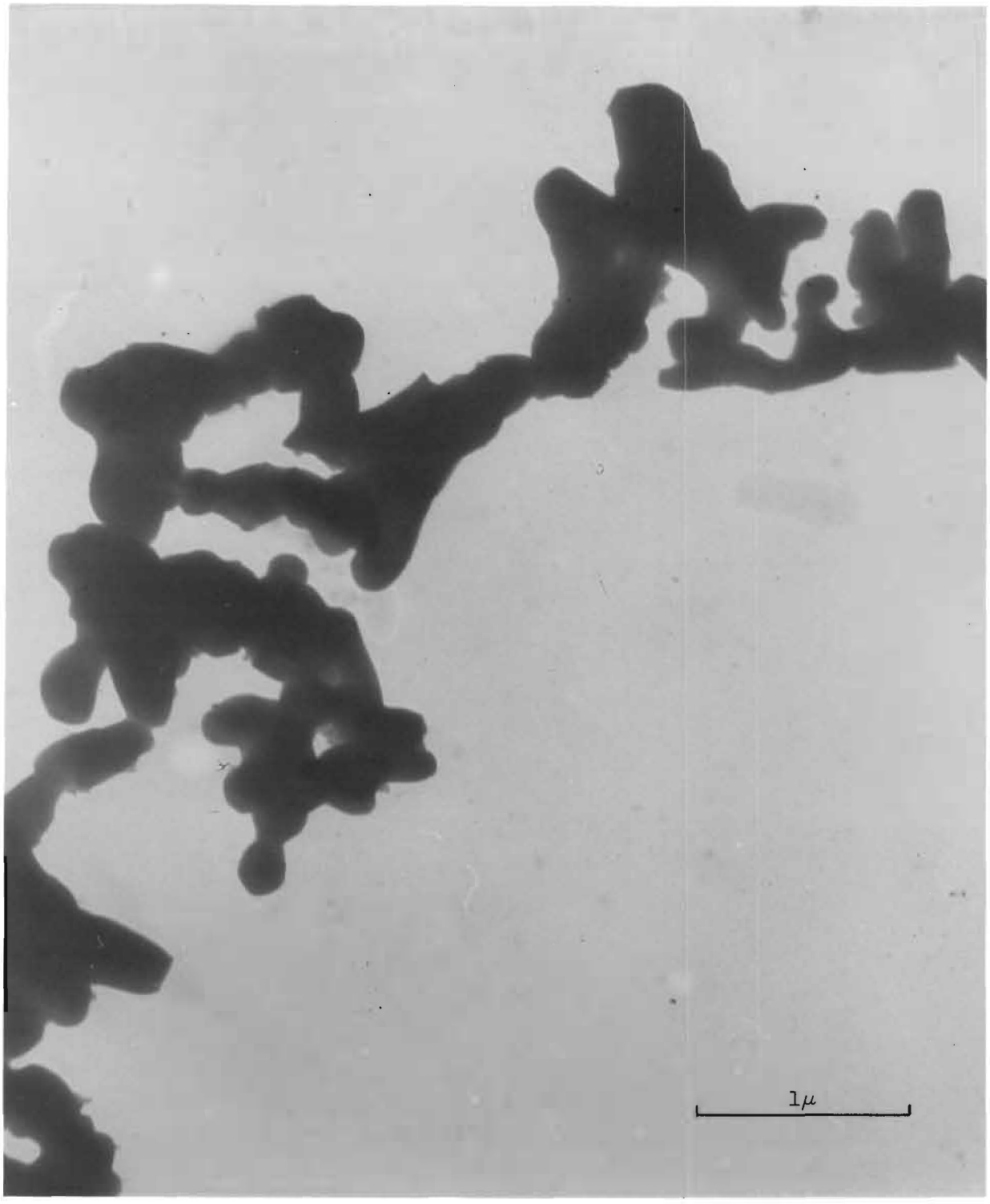

Figure 2. Agglomerated Alumina.

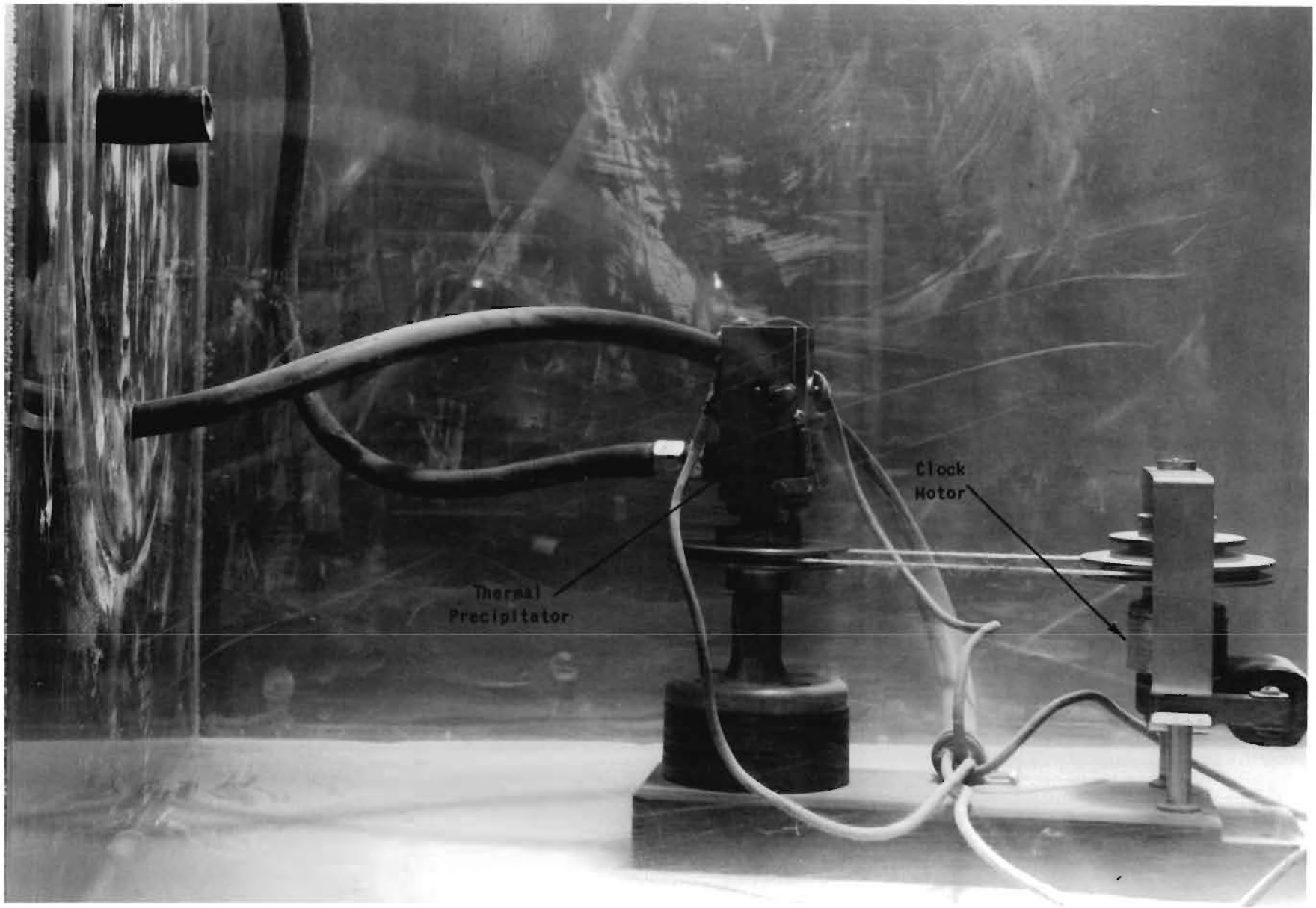

Figure 3. Thermal Precipitator in Aerosol Chamber. Side View.

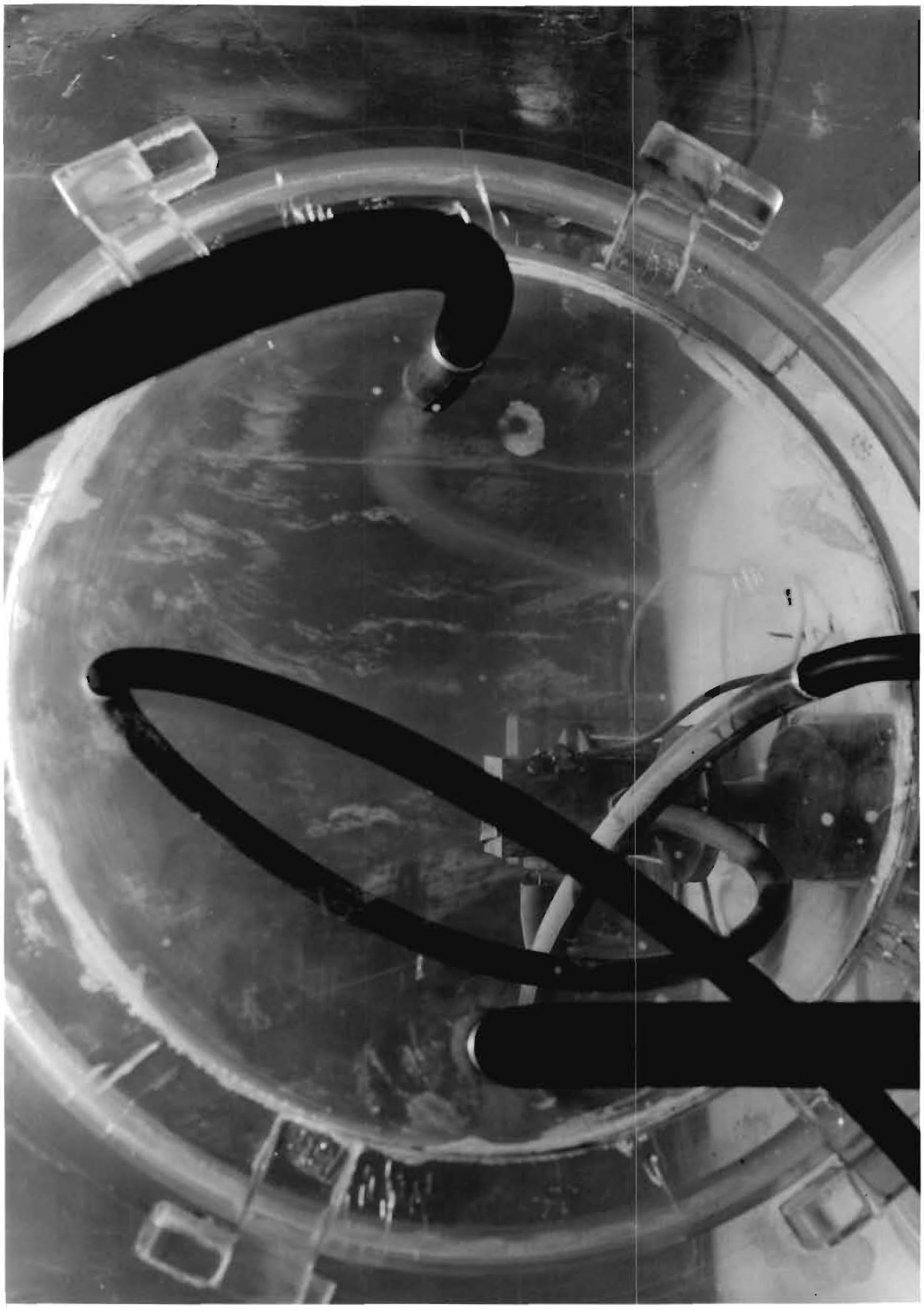

Figure 4. Thermal Precipitator in Chamber. Front View.

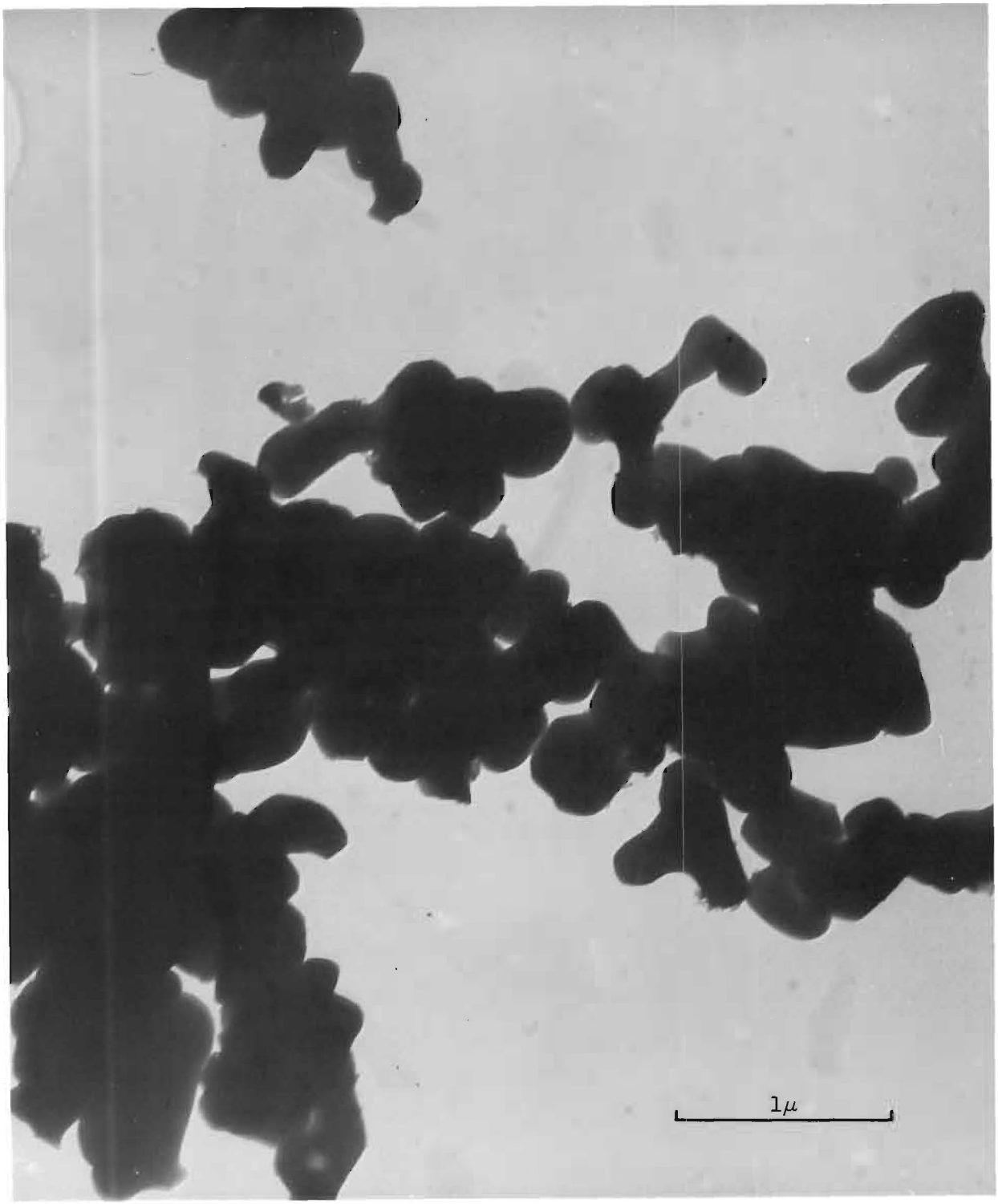

Figure 5. Agglomerated Alumina after Passage through an Electrical Discharge.

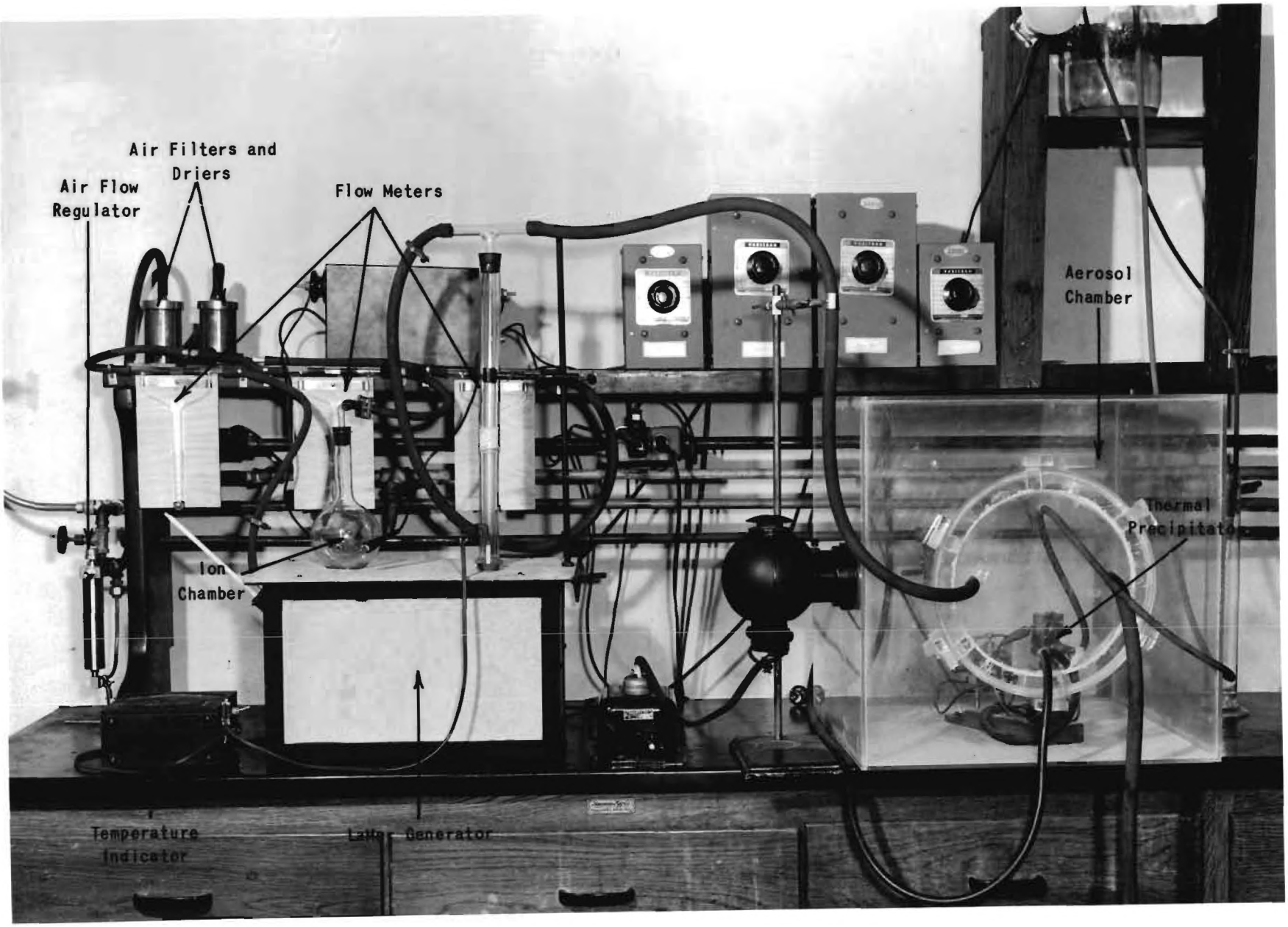

Figure 6. LaMer Aerosol Generator and Aerosol Chamber.

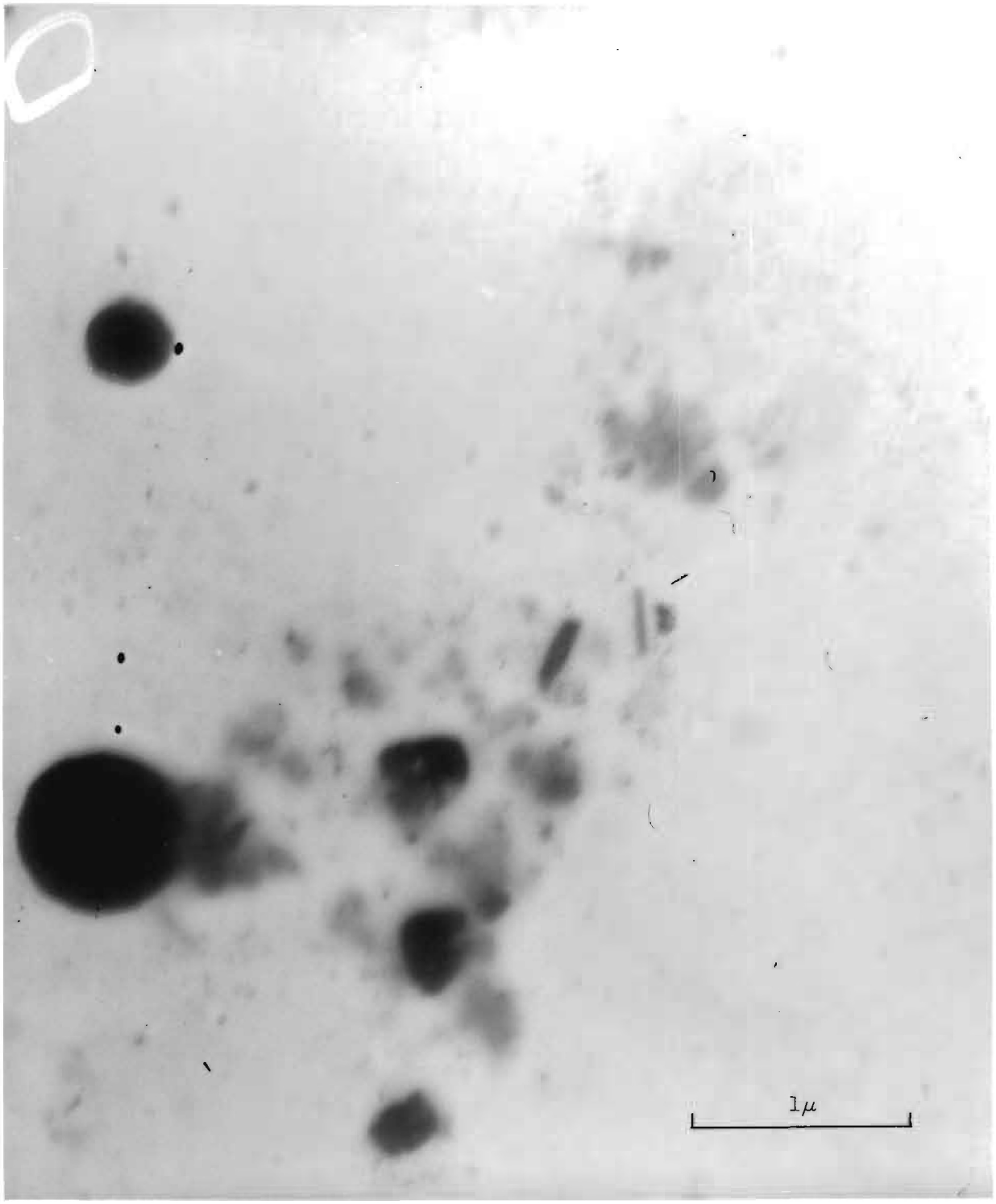

Figure 7. Stearic Acid Particles Probably Showing Melting As A Result of Thermal Precipitation.

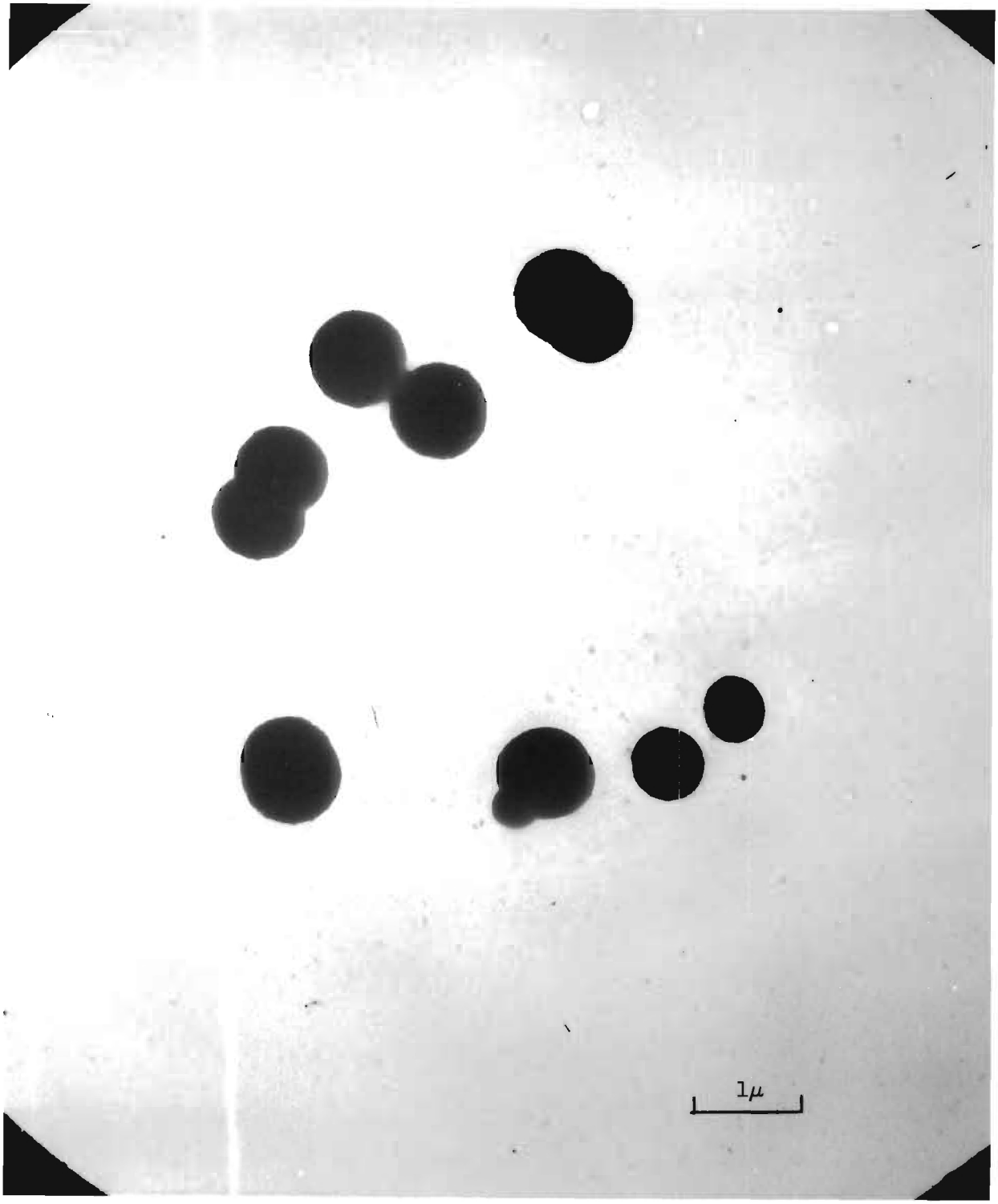

Figure 8. Stearic Acid Particles.

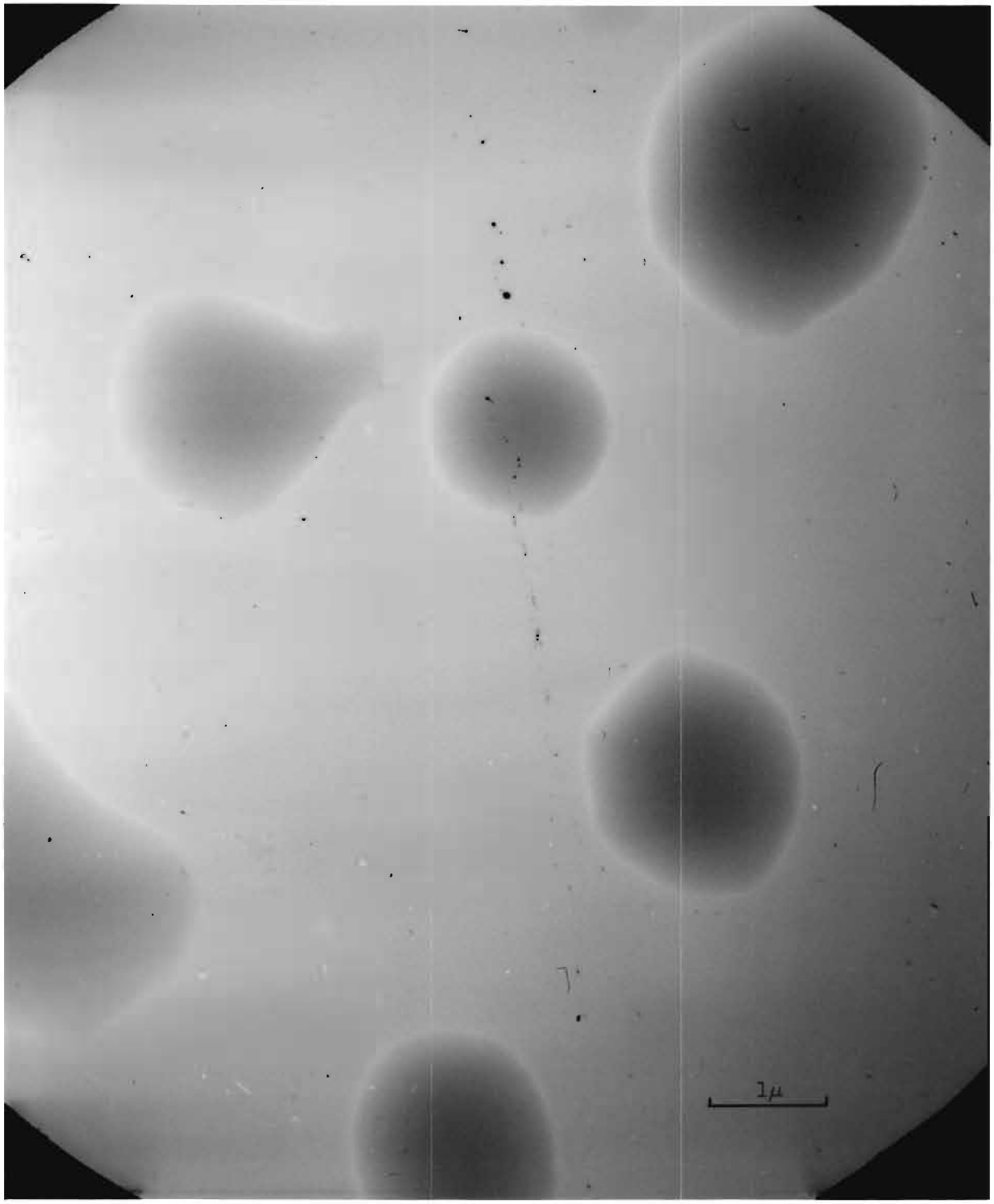

Figure 9. Stearic Acid Particles Probably Melted by Thermal Precipitation.

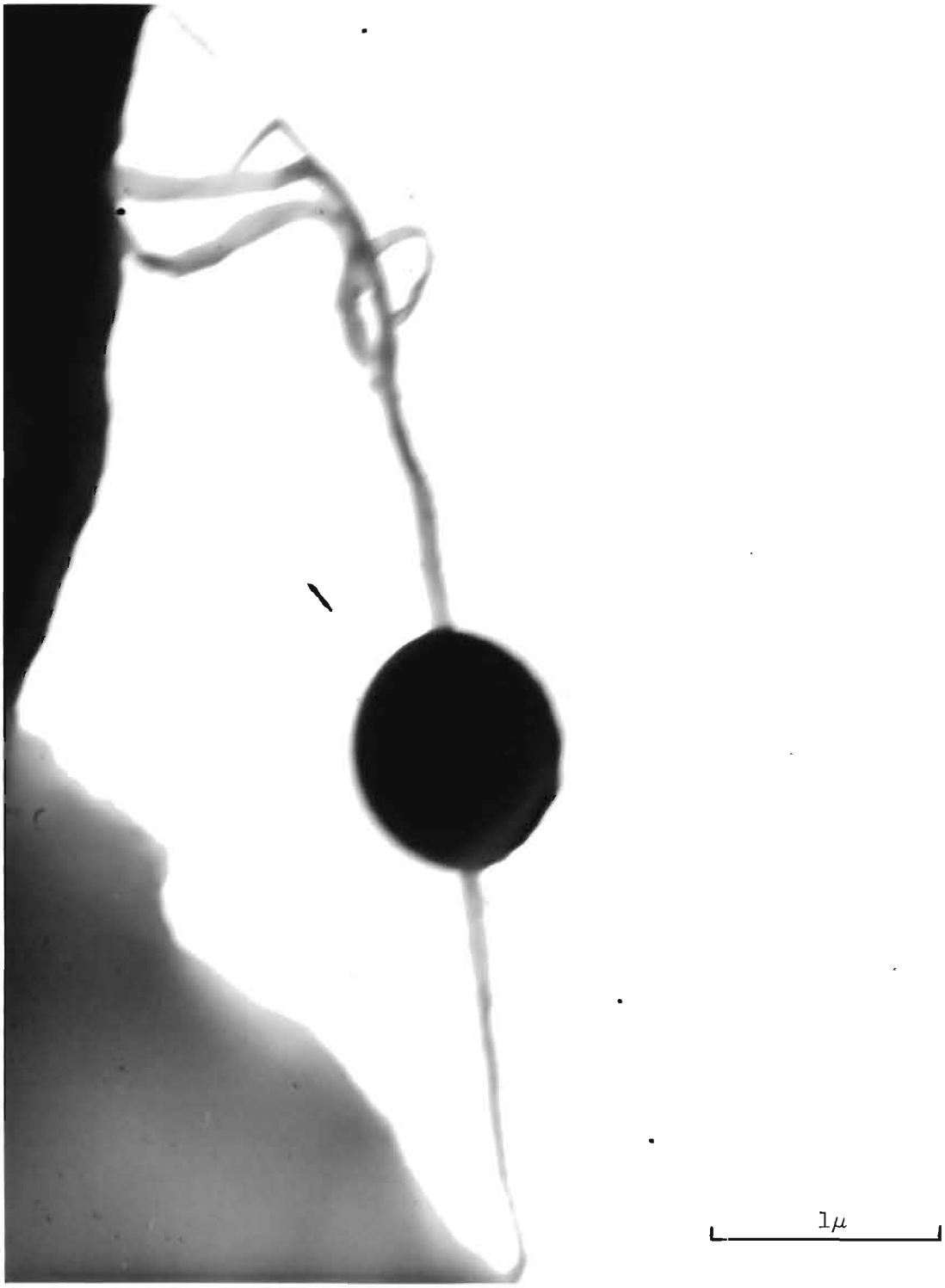

Figure 10. A Stearic Acid Particle Collected on Lens Tissue.

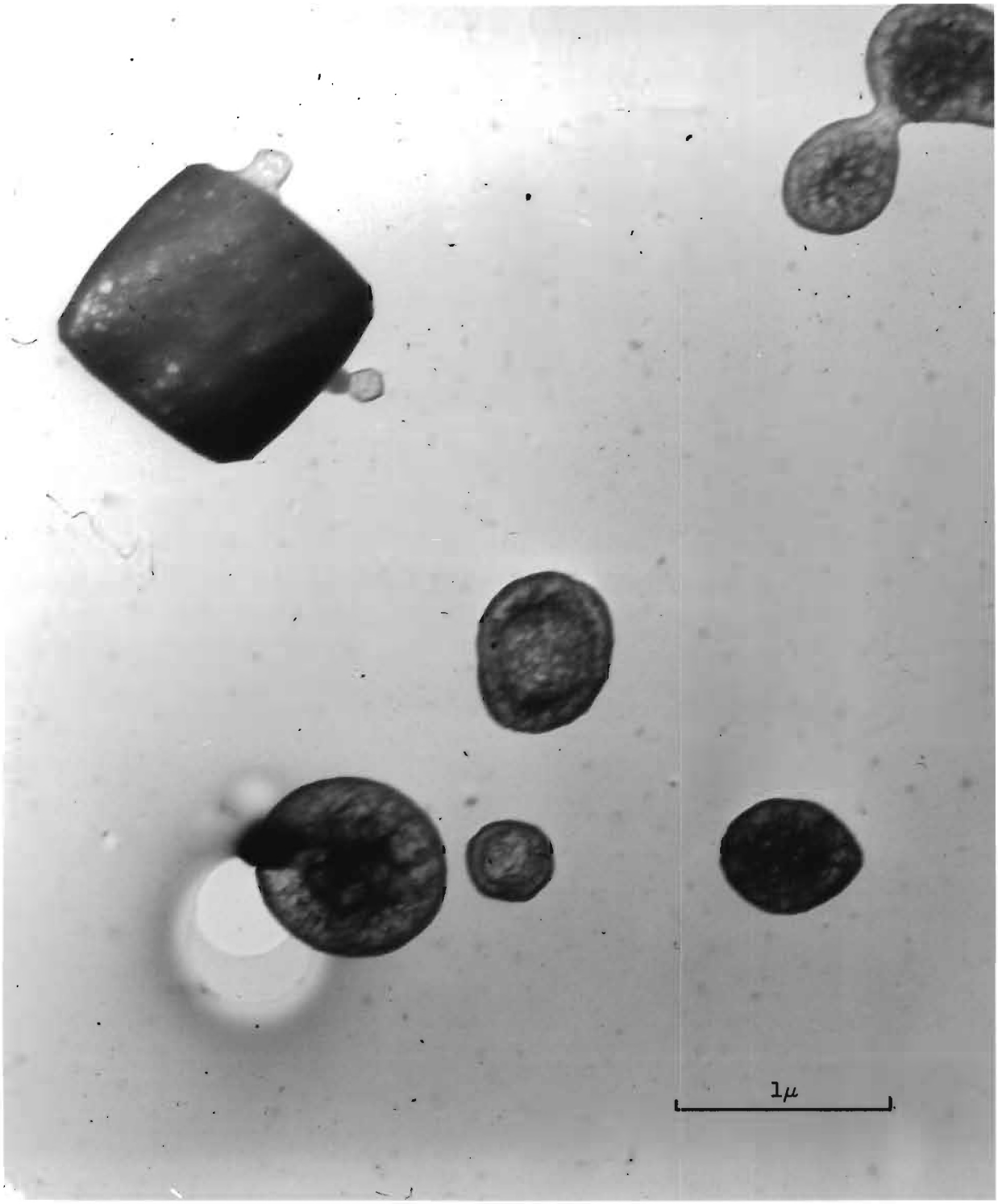

Figure 11. Ammonium Chloride Particles Produced by Mixing Ammonia and Hydrochloric Acid Vapors.

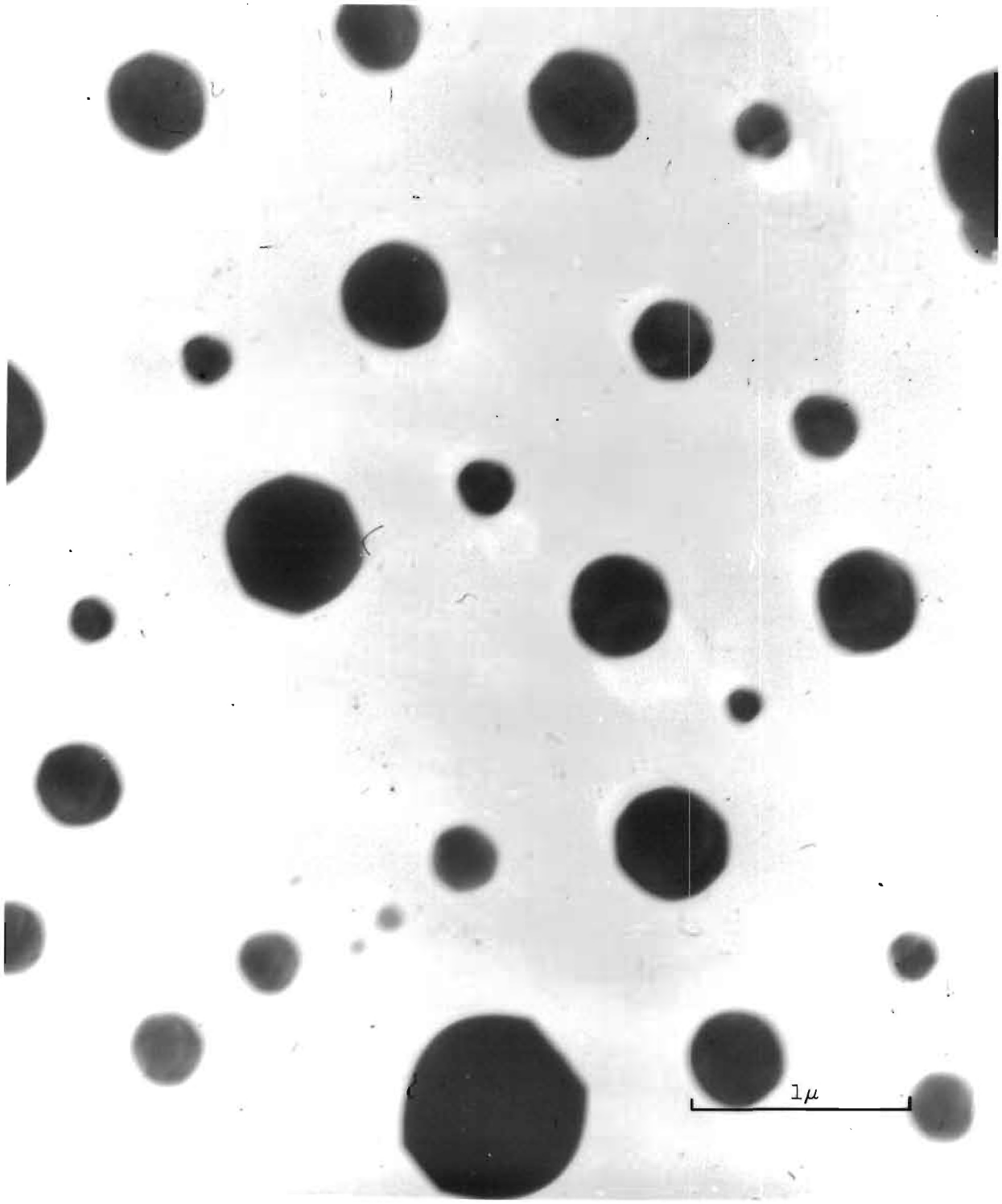

Figure 12. Ammonium Chloride Particles after a Brief Exposure to the Electron Beam of An Electron Microscope.

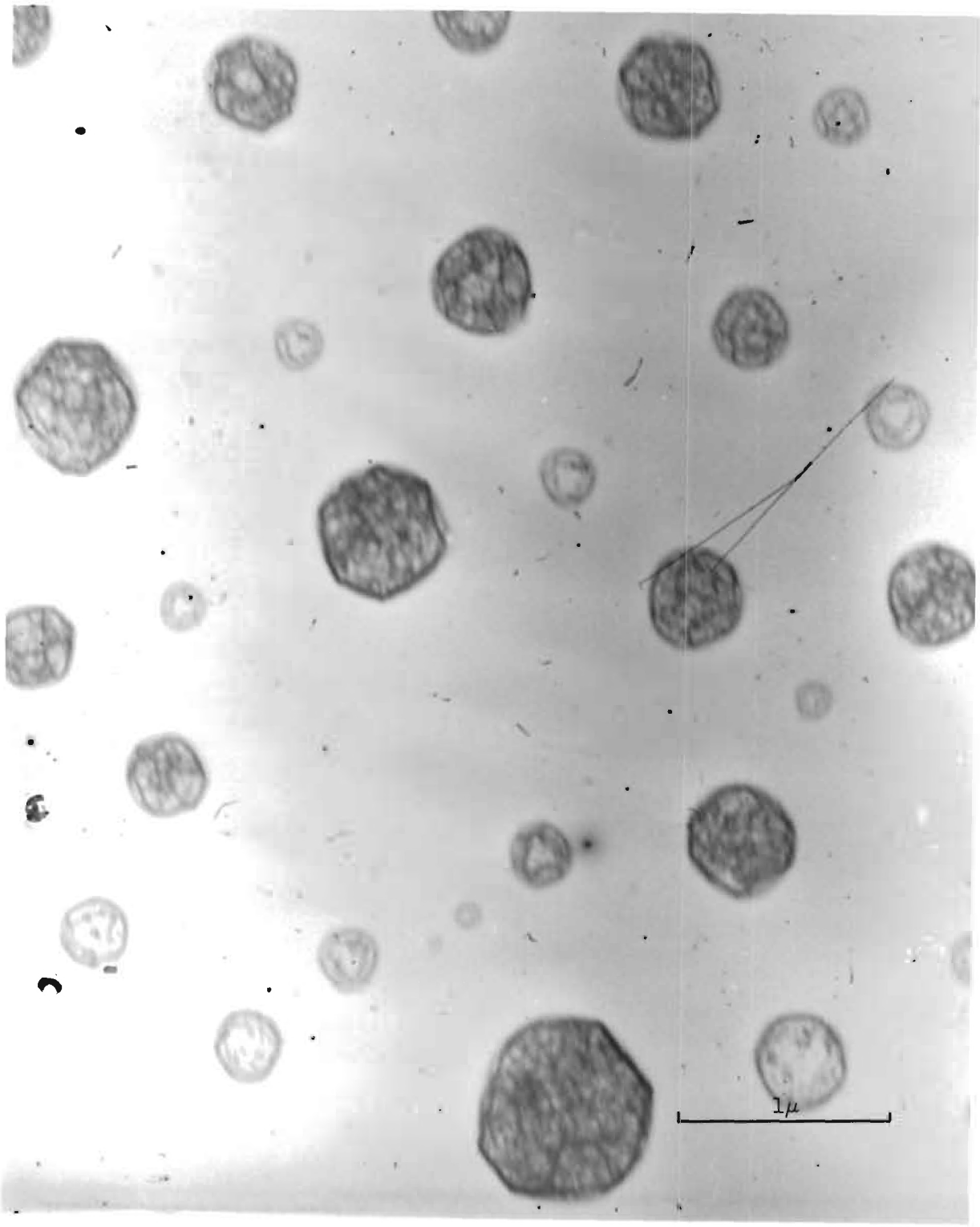

Figure 13. Ammonium Chloride Particles after A One-Minute Exposure to the Electron Beam of An Electron Microscope.

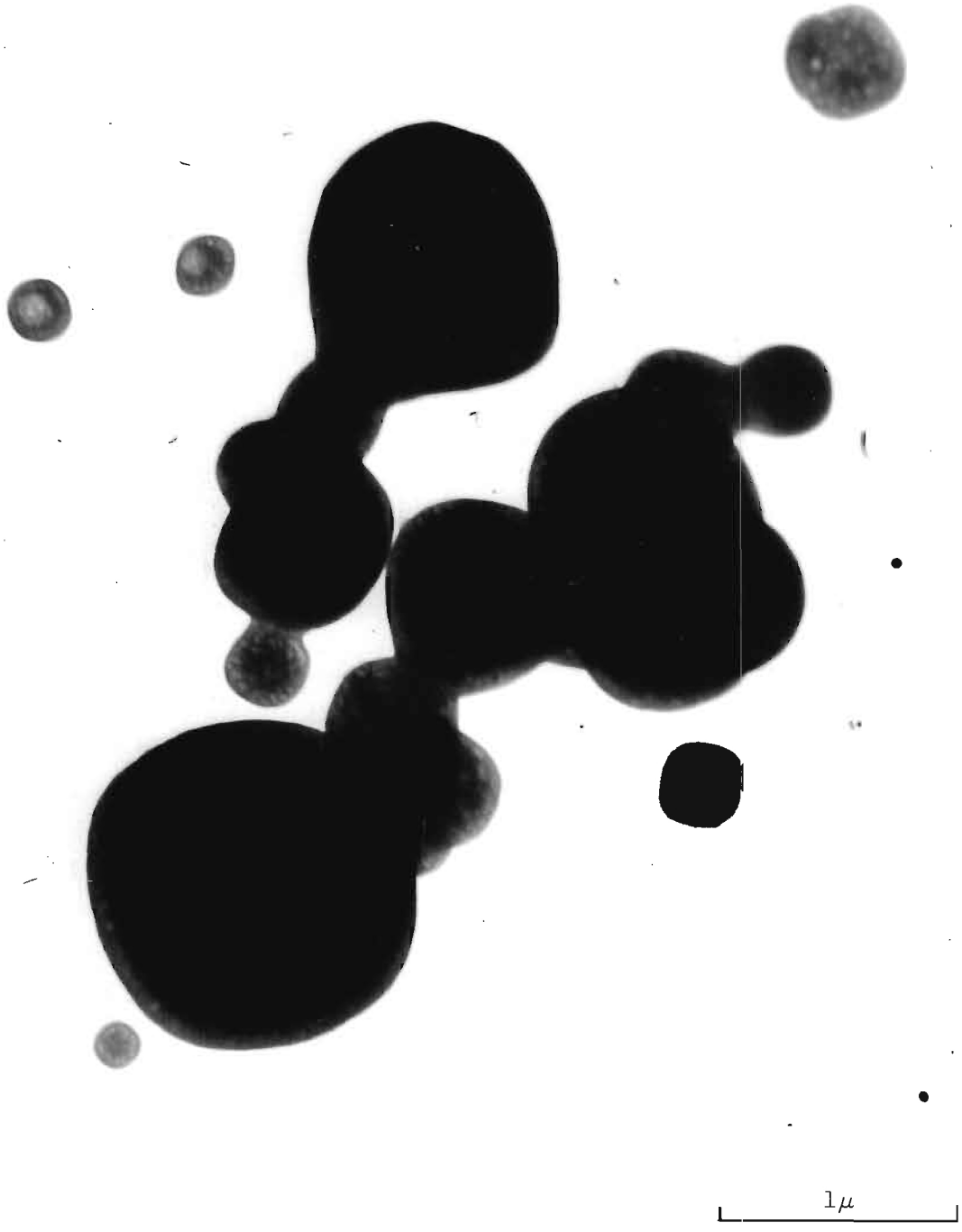

Figure 14. Ammonium Chloride Particles after A Brief Exposure to the Electron Beam of An Electron Microscope. Particles were Produced by Vapor-Mixing Process.

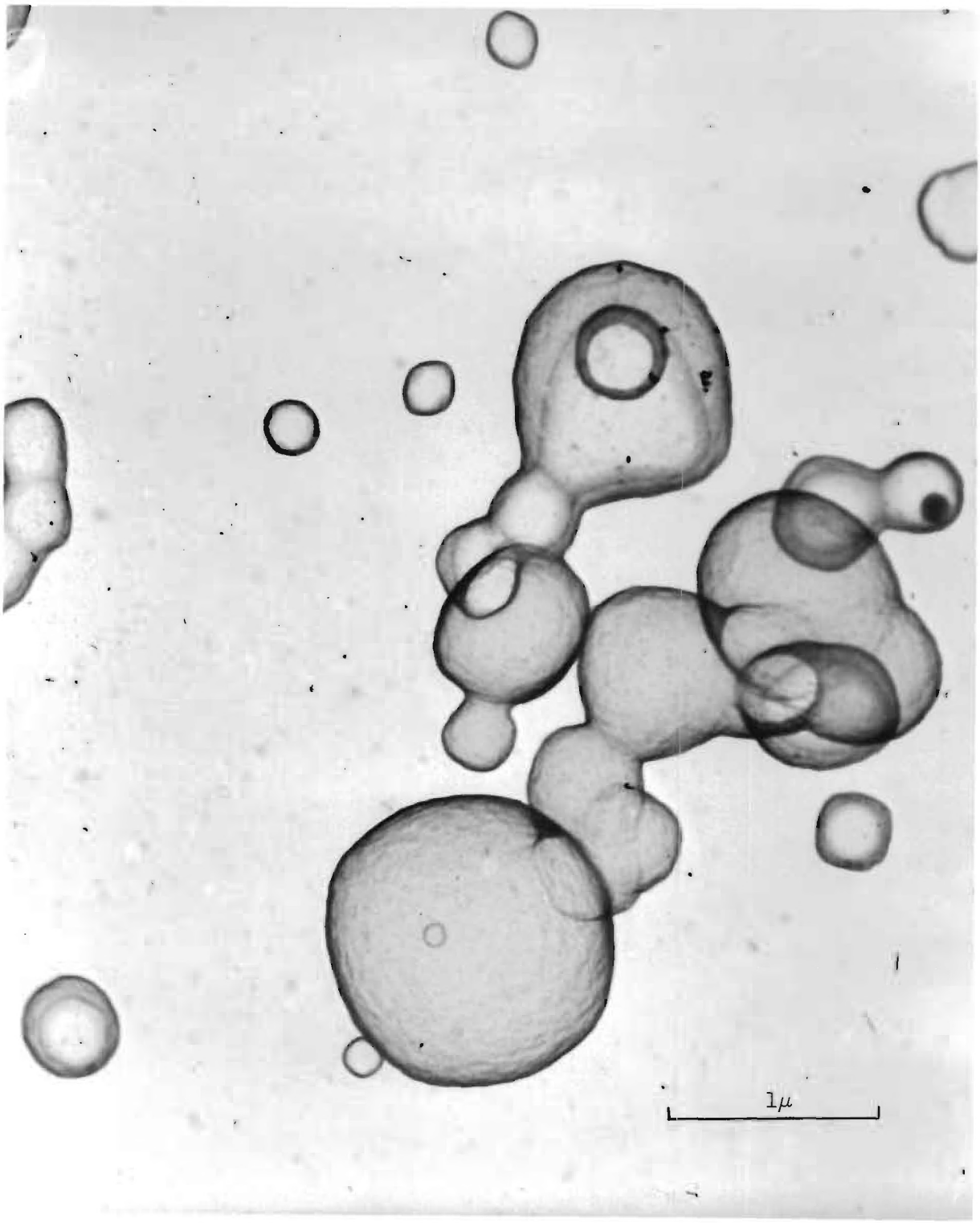

Figure 15. Ammonium Chloride Particles after A Three-Minute Exposure to the Electron Beam of An Electron Microscope. Particles Were Produced by Vapor-Mixing Process.

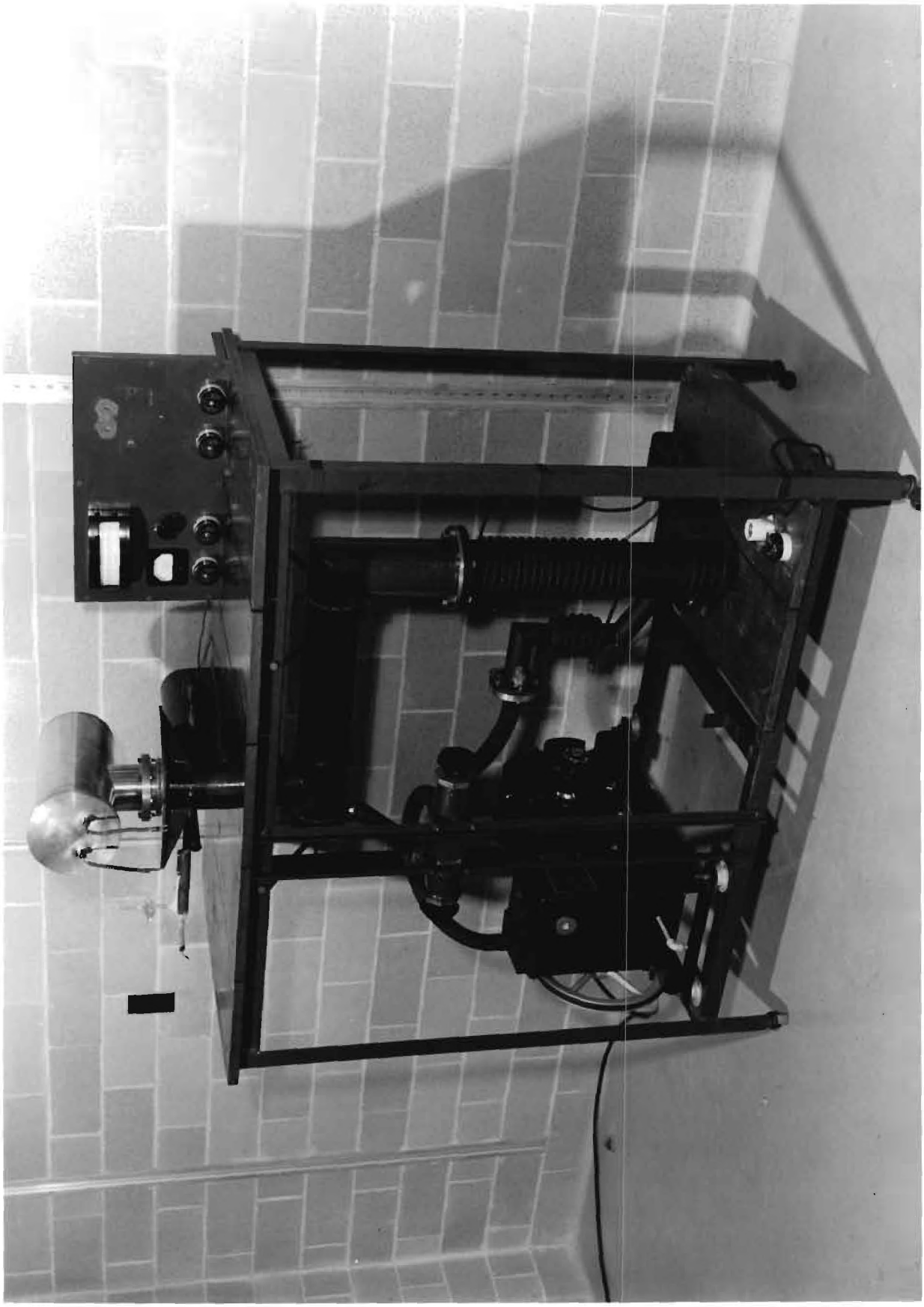

Figure 16. Shadowing Apparatus.

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MARCH 14, 1951

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MARCH 14, 1951

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This Report Contains 21 Pages

I. SUMMARY

Factors which affect the aggregation of aerosols were investigated. It was concluded that electrical charge is of relatively little importance in producing aggregation but does determine the orientation of the aggregated particles. The aggregative effect of dipolar vapors was established, and apparatus and techniques have been developed to investigate completely the associated phenomena. A method of producing an aerosol in which all particles are dipolar has been found.

Scrutiny of the scientific literature on the subject of aerosols reveals that a disturbing amount of research has been carried out in the Laboratory of Aerosols, Karpov Institute of Physical Chemistry in Moscow in recent years.

II. INTRODUCTION

This investigation is primarily concerned with the factors affecting the aggregation of aerosols--particularly electrical charge and concentration. Special interest has been directed toward the phenomenon of aggregation itself. Early in the investigation it was felt that a determination of the basic factors contributing to aggregation would add greatly to knowledge of the control of airborne bacteria and toxicants which might be used in wartime.

The amount of information available on the subject is scanty. However, it is to be noted that much of the work done in this connection is contained in the Russian scientific literature. This country is far behind the Russians in this field, and a perusal of their contributions shows that their interest is more than purely academic.

If harmful aerosols can be aggregated by any means, the problem of their collection is made much easier. One of the difficulties which face this country, in event harmful aerosols (bacteria, gas carriers, radioactive particles) are used, is their elimination from air in areas in which people are congregated, especially in industries. Thus, large volumes of air must be cleaned, and greater certainty of aerosol removal would be achieved if the injurious aerosols could be first aggregated by any suitable means.

It is felt that this is the primary intent of the Russians, and that all efforts must be directed toward a similar objective. While the actions of electrostatic charges present in a cloud have yielded little to indicate that they are effective in causing aggregation, it has been found — as the Russians have found — that violent agitation and the introduction of polarized vapors are effective.

There is one other aspect which should be mentioned regarding this objective. If the mechanisms of aggregation can be understood, then the matter of deaggregation will have been solved also, a desirable objective in other connections.

III. THEORY OF AGGREGATION

The following paragraphs outline the present state of knowledge pertaining to aerosol aggregation. The exact mechanisms of aggregation or coalescence are not well understood. It has been thought that the particles are attracted to each other electrostatically or come together as a result of collisions due to their random motion (Brownian motion) and to thermal and mechanical agitation. It may be interesting to note that coagulation by sound waves is at least partially due to the pressure decrease produced in the space

between the particles (in accordance with Bernoulli's principle) as the pressure waves pass. As will be shown later, while particles rarely come together without external influences, when they do coalesce, they exhibit polar characteristics, i.e., they form long chains.

The theory of aggregation of monodisperse systems has been worked out by von Smoluchowski[1] who derived the expression for the concentration

$$n = \frac{n_o}{1 + 4\pi D R n_o t}, \qquad (1)$$

where n = concentration at any time,

n_o = initial concentration,

D = the diffusion coefficient,

R = the "active" radius of the particles involved, and

t = time.

The development given by von Smoluchowski stipulates that, once coalescence takes place between two particles, a third, fourth, etc. particle coalesces with them and there is no tendency to separate. Equation (1) can be put into the form

$$-\frac{dn}{dt} = 4\pi D R n^2 = K n^2, \qquad (2)$$

where K can be called the coefficient of coalescence. Equation (2) has been tested by Whytlaw-Gray and collaborators[2] and found to represent certain experimental data.

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(1) von Smoluchowski, M., "Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Lösungen." Zeitschr. phys. Chem. 92, 129-68 (1917).

(2) Whytlaw-Gray, R., Cawood, W., and Patterson, H. S., "A Sedimentation Method of Finding the Number of Particles in Smokes." Trans. Faraday Soc. 32 (Part 8) 1055-59 (1936).

An almost analogous expression has been obtained by Tunitskiĭ[3] relative to the decrease in the amount of charge on a monodisperse system as coalescence takes place. If Z is the charge at time t,

$$Z = \frac{Z_o}{1 + 1/2K\ n_o\ t}, \qquad (3)$$

where Z_o = total initial charge,

and the other symbols are as before. This is derived on the assumption that the charge on each particle is the same at time $t = 0$. Tunitskiĭ also gives the distribution of charges of particles of size x as

$$F(Z,x) = K\ \frac{2\ b\ x\ Z}{e^{2bxZ} - 1} \qquad (4)$$

where $b = \epsilon^2/4rkT$,

x = particle size at any time,

r = initial particle size,

ϵ = the value of the fundamental charge,

k = Boltzmann's constant, and

T = absolute temperature.

No expression has been derived either for coalescence or charge when the initial distribution is polydisperse.

It does not appear from these investigations that electrical charge is important in causing particle aggregation. Results show that, even at relatively high concentrations, monodisperse systems persist after long periods of time. The particles of stearic acid (almost 0.75 microns in diameter) and ammonium chloride showed little tendency to aggregate unless they were violently agitated or were influenced by certain organic vapors. The possibility that all the charged particles were of like charge must be considered in relation

(3) Tunitskiĭ, N., "Coagulation of Weakly Charged Aerosols." J. Phys. Chem. (U.S.S.R.) 13, 1141-44 (1939).

to the persistence of dispersion. It is well established that the effect of electrical charge does not extend very far beyond the surface of a particle (inverse square law), and there is reason to suppose that Brownian motion and thermal turbulence are of greater importance in so far as aggregation is concerned.

As an example of the requirements for aggregation of particles, assume that the effect of an electrostatic field does not extend much beyond three particle diameters if aggregation is to take place. Then, if the particles have a diameter of one micron and an initial concentration of the order of 10^{11} particles per ml., a mean distance between each of about 5.5 microns is required for aggregation. Such concentrations are so dense that aggregation by direct contact due to thermal turbulence is more probable. It will be seen from what follows later in this report that the particles studied are probably electrically neutral and are dipolar.

Concerning the forces that hold the particles together once they have come into contact with others, the surface energy theory of Bradley[4] and the theory of Beischer,[5] which considers van der Waals' forces, surface diffusion and electric forces, have been proposed. Bradley considers that the nature of the binding force is one of surface energy. He finds that the surface energy, σ, is of the order of 10^{-4} dynes per cm. Thus, for particles of one micron in diameter, the binding force is

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(4) Bradley, R. S., "The Cohesion between Smoke Particles." Trans. Faraday Soc. 32 (Part 8) 1088-90 (1936).

(5) Beischer, D., "Oriented Coagulation in Aerosols. III. Physical Strength of Aerosol Sediments." Kolloid Z. 89, 214-19 (1939).

$$F = 2\pi r\sigma = 2\pi \times 1/2 \times 10^{-4} \times 10^{-4}$$

$$= 3.1 \times 10^{-8} \text{ dynes.}$$

The general expression for the binding force as obtained by Bradley is

$$F = \frac{4\pi r_1 \ r_2}{r_1 + r_2} \cdot \sigma \ , \qquad (5)$$

where the r's are the radii of the particles aggregating, indicating that the forces are greater when one of the particles is smaller than the other. Thus, once aggregation has started, additional particles will be bound more tightly. In other words, the aggregated aerosol is more stable as the individual particles increase in size. Aggregation by means of sound results in chains of many particles and few two- or three-particle chains.

IV. EXPERIMENTAL WORK

It was found that the presence of naphthalene vapor in particular affected the coagulation of even mildly agitated ammonium chloride aerosols. In these tests the aerosol was generated and introduced into the plastic chamber as described under "Experimental Work" in Quarterly Report No. 2. The system finally devised for introducing vapor into the aerosol chamber consisted of a glass container connecting with the line between the La Mer aerosol generator and the chamber. The temperature and rate of vaporization were thus controlled outside the chamber and thorough mixing with the aerosol was assured. The aerosol was sampled with the thermal precipitator described under "Equipment" in Quarterly Report No. 1.

In order to produce more violent agitation while avoiding the effects of actual contact of the particles with the stirrer fan

blades and walls of the chamber and because some work[6] indicated the existence of a minimum degree of agitation, an ultrasonic generator was built. Essentially, the design developed by St. Clair[7] was followed. A picture of the present apparatus is shown in Figure 1 of the appendix and its circuit diagram is given in Figure 2. The wave pattern about the sound generator is shown in Figure 3. Results of preliminary tests with this equipment are given in the following section.

V. RESULTS

The aggregation produced in an ammonium chloride aerosol by 15 minutes' agitation by the small fan in the presence of naphthalene vapor is shown in Figure 4. The same agitation alone produced no aggregation. Phenol and alcohol vapors produced no detectable aggregation with this agitation. The effects of vapors of any kind were undetected without agitation; however, this probably indicates only that little chance for contact occurred.

The formation of chain-like aggregates by ultrasonic vibrations is shown in Figures 5 through 10. Examination of these figures shows that the aggregates are always chain-like, and, in the case of short chains, are quite straight, with the particles diametrically aligned. Straight chains as long as one quarter of one inch, composed of

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(6) Piazza, J., "Experiments for the Precipitation of Aerosols." Anales Soc. Cient. Argentina 137, 49-81 (1944).

(7) St. Clair, H. W., "Sonic Flocculator as a Fume Settler: Theory and Practice." U. S. Bur. Mines Rept. Investigations, 3400, 51-64 (1938).

hundreds of particles, have been observed, but these are most often composed of straight segments only. The area over which the particles are joined appears to be the result of fusion by surface diffusion as proposed by Beischer[8] or perhaps by solution and evaporation in the presence of the moisture in the atmosphere.

It would seem that the concepts of aggregation must be modified to include this preferred orientation of particles which is probably the result of forces of an electrical nature. This effect adds strength to the theory that most or perhaps all particles are somewhat dipolar but do not necessarily possess an excess of either kind of charge.

Thus far, the studies indicate that electrical charge does not influence aggregation to any extent, except that, when the particles come into close proximity as a result of other factors, electrical forces determine the orientation of the aggregate.

All activities are well under way toward securing valuable data on the phenomena of aggregation. In addition, the following improvements in technique have been achieved in the course of the project:

(1) Development of methods of producing monodisperse and polydisperse aerosols over a wide range of concentrations.

(2) Development of a method of sampling of great utility for studying aggregation.

(3) Development of a technique of introducing polarized vapors which cause aggregation.

(4) Development of means of making and introducing polarized aerosols (electrets) which may greatly enhance aggregation.

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(8) Loc. cit.

(5) Development of a method for controlling degree of agitation to determine effect on aggregation.

A great deal of effort and time has been required to gather the data needed in interpreting the phenomena of aggregation, but most of the necessary tools are now available.

VI. FUTURE PROGRAM

Since it has been resolved that the electrical charge present on a cloud has little bearing on aggregation, research will be continued along the following lines:

(1) Measuring the influence of various concentrations of organic vapors on rate of aggregation in an aerosol system.

(2) Determining the effect of agitation on aggregation.

(3) Determining the effect of polarized aerosols (electrets) on aggregation, i.e., use of other aerosols to assist aggregation.

(4) Using the methods outlined in (1), (2), and (3) together so as to determine the optimum conditions leading to aggregation when they are combined.

In order to carry out this program, work is under way on the following:

(1) Procuring a Tyndall meter.

(2) Adapting a high voltage source to produce electrets.

(3) Altering the cooling system of the magnetostriction oscillator so that water vapor will not be introduced into the aerosol chamber except as desired.

Respectfully submitted:

J. M. DallaValle,
Project Director

Clyde Orr, Jr.,
Research Assistant

L. A. Woodward,
Research Associate

Approved:

Gerald A. Rosselot, Director
State Engineering Experiment Station

VII. APPENDIX

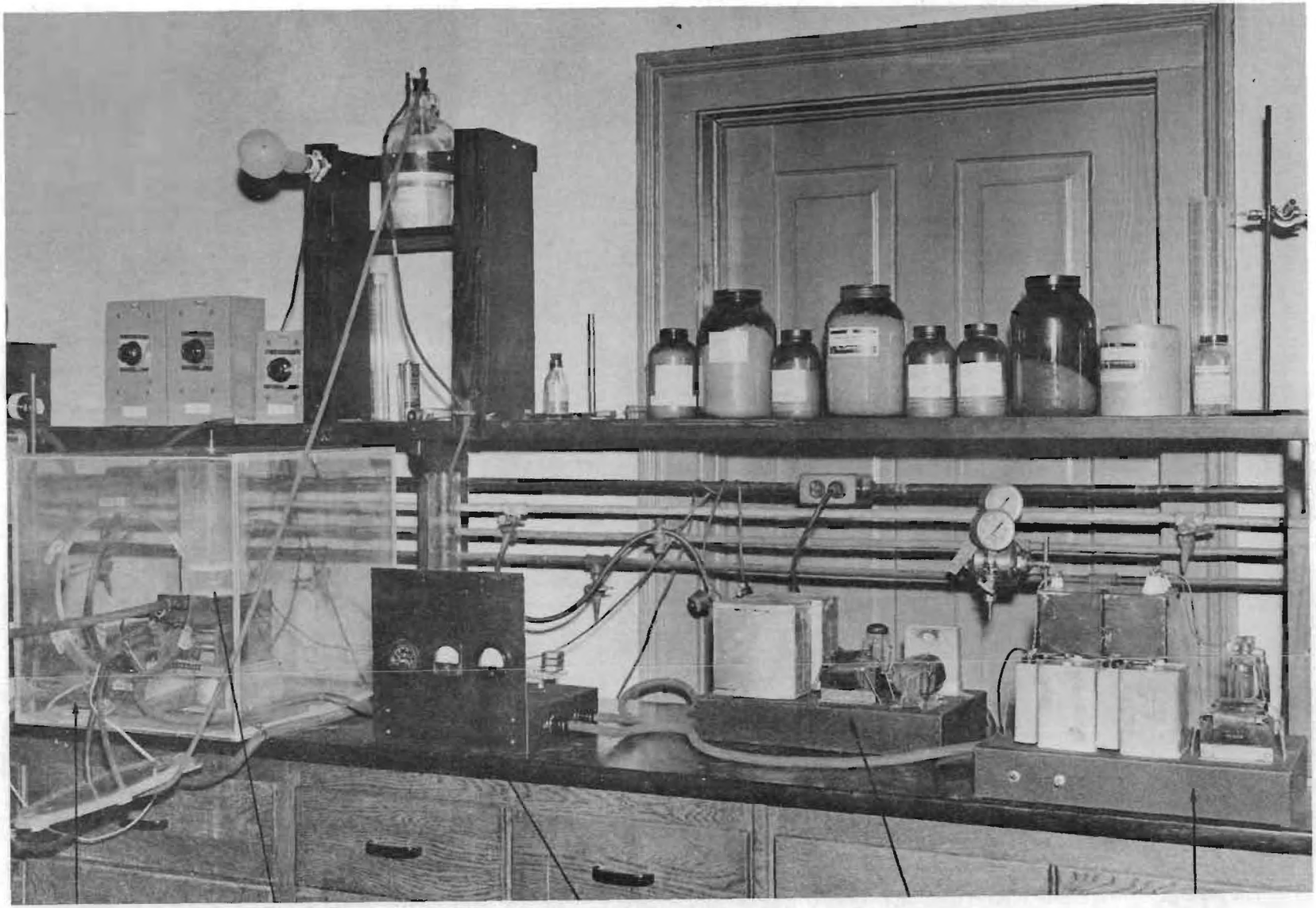

Figure 1. Magnetostriction Oscillator and Aerosol Chamber.

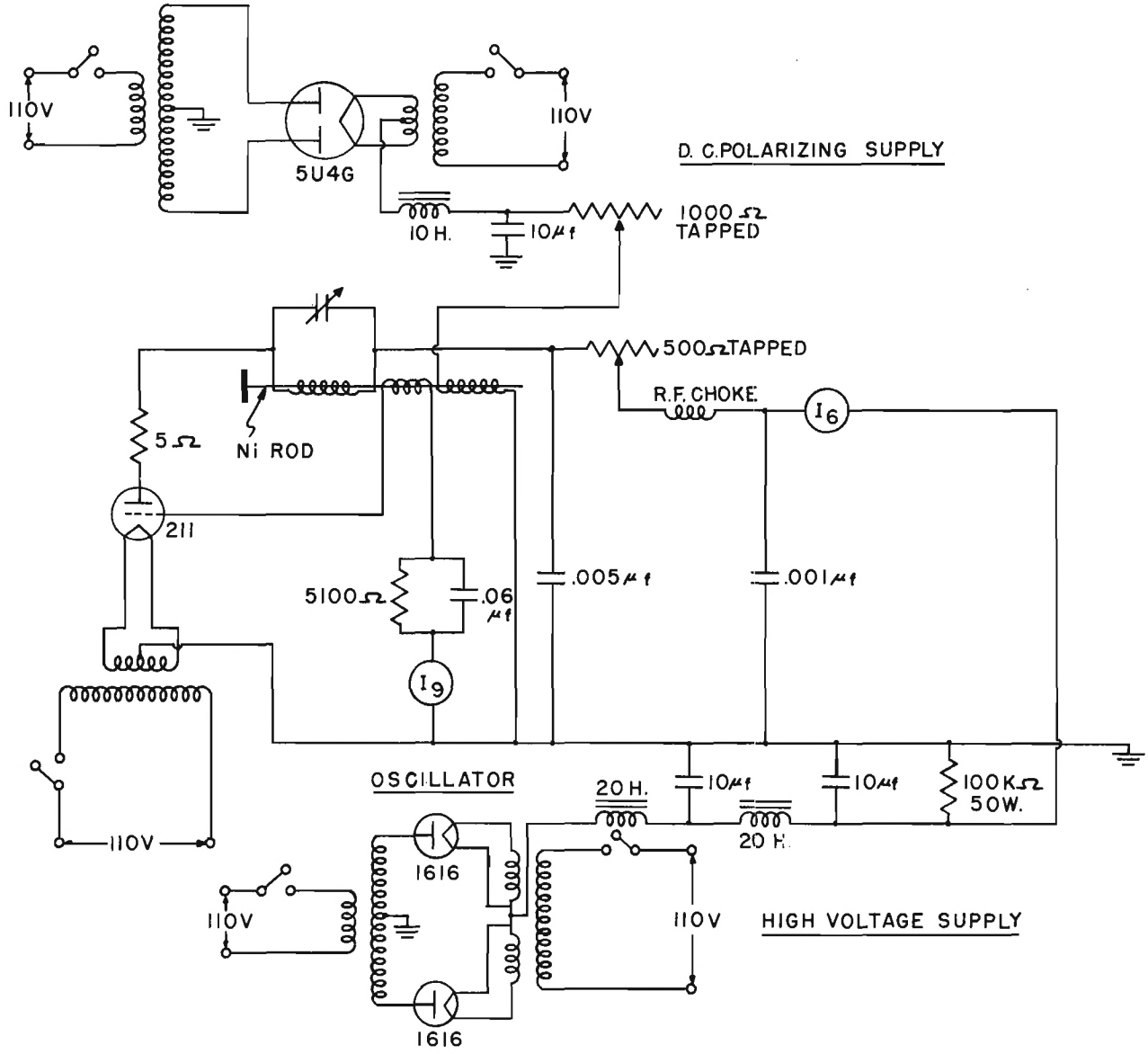

Figure 2. Magnetostriction Oscillator Circuit Diagram.

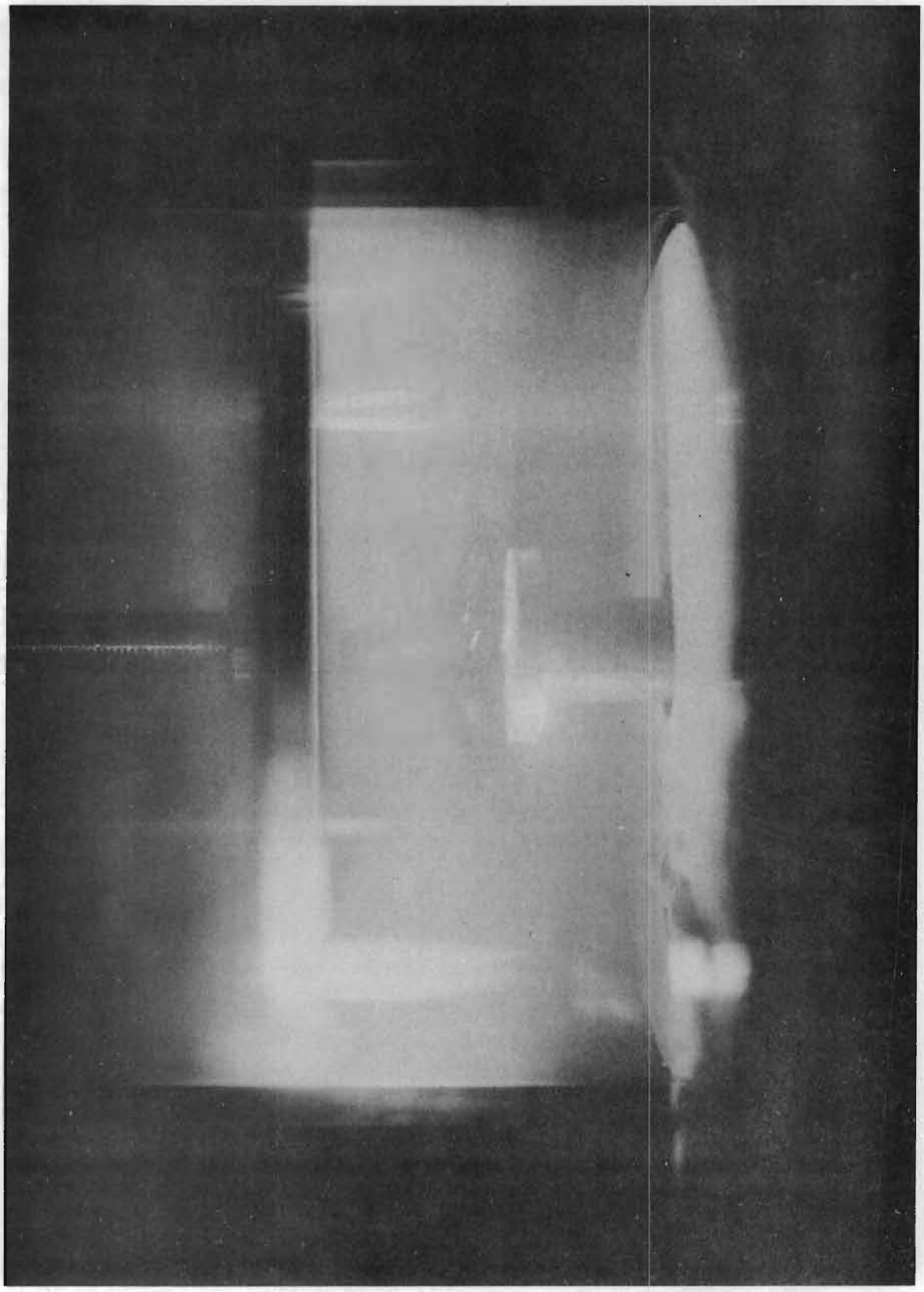

Figure 3. Wave Pattern Produced by Sound Generation.

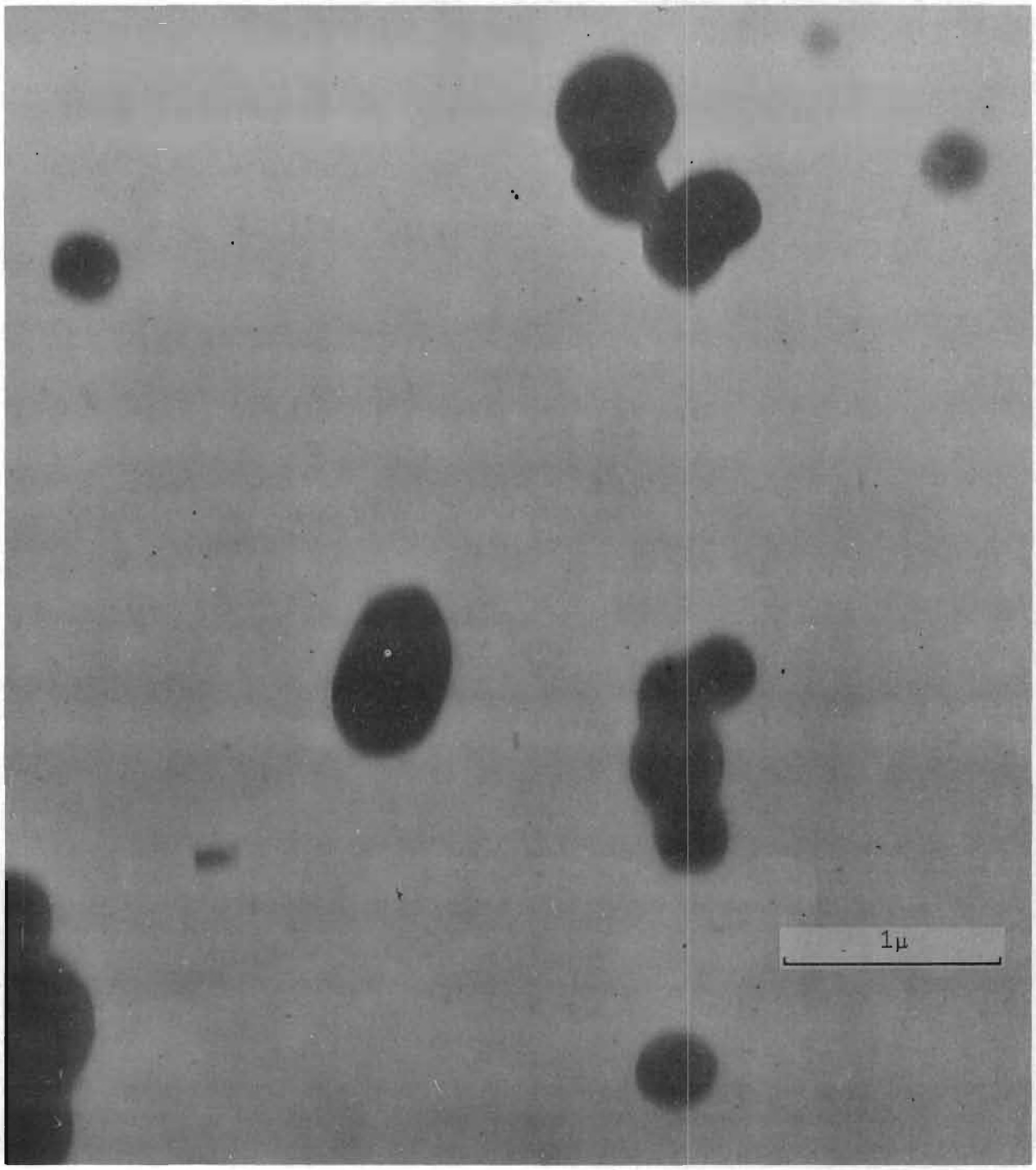

Figure 4. Ammonium Chloride Particles Aggregated by Naphthalene Vapor.

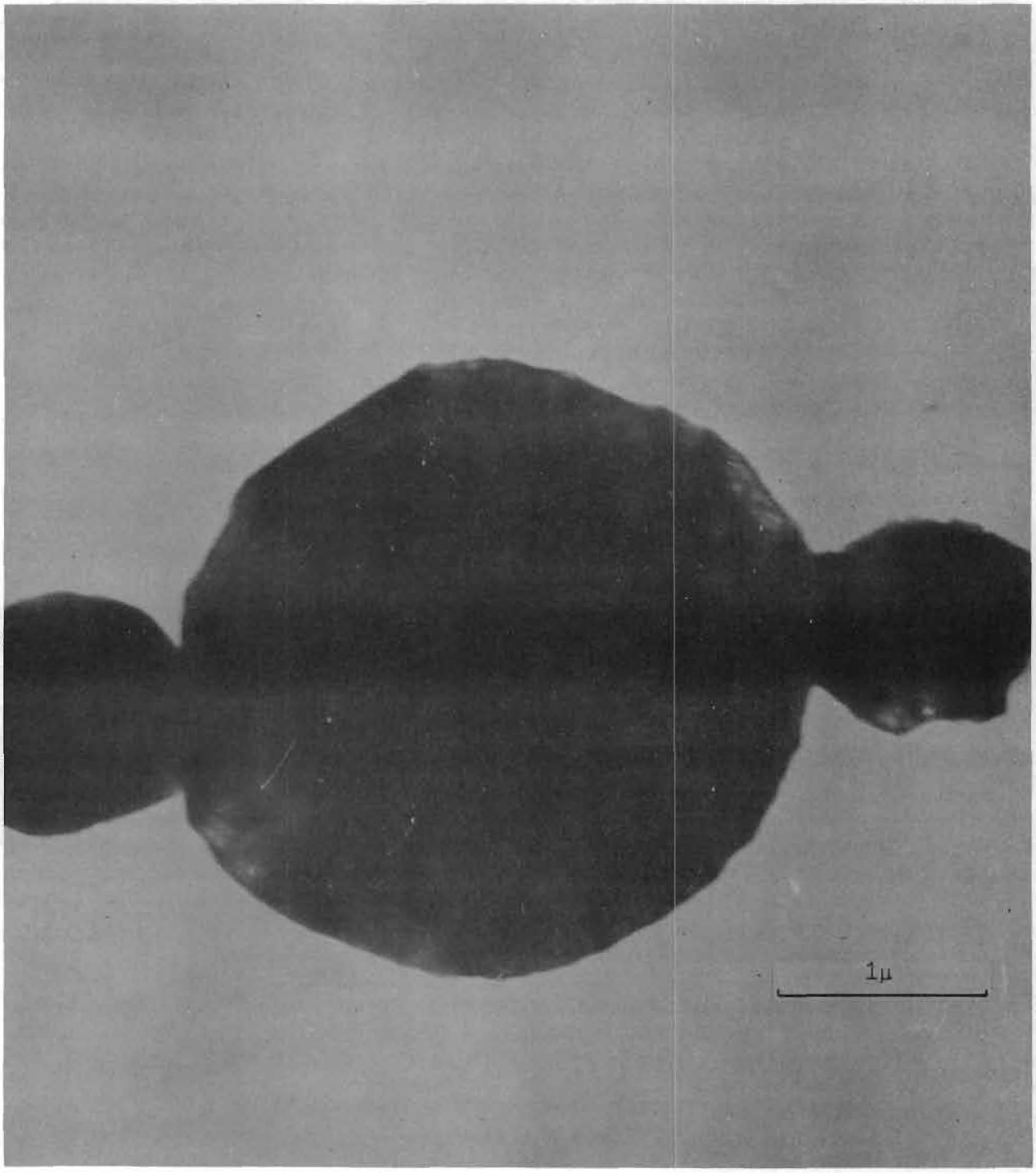

Figure 5. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

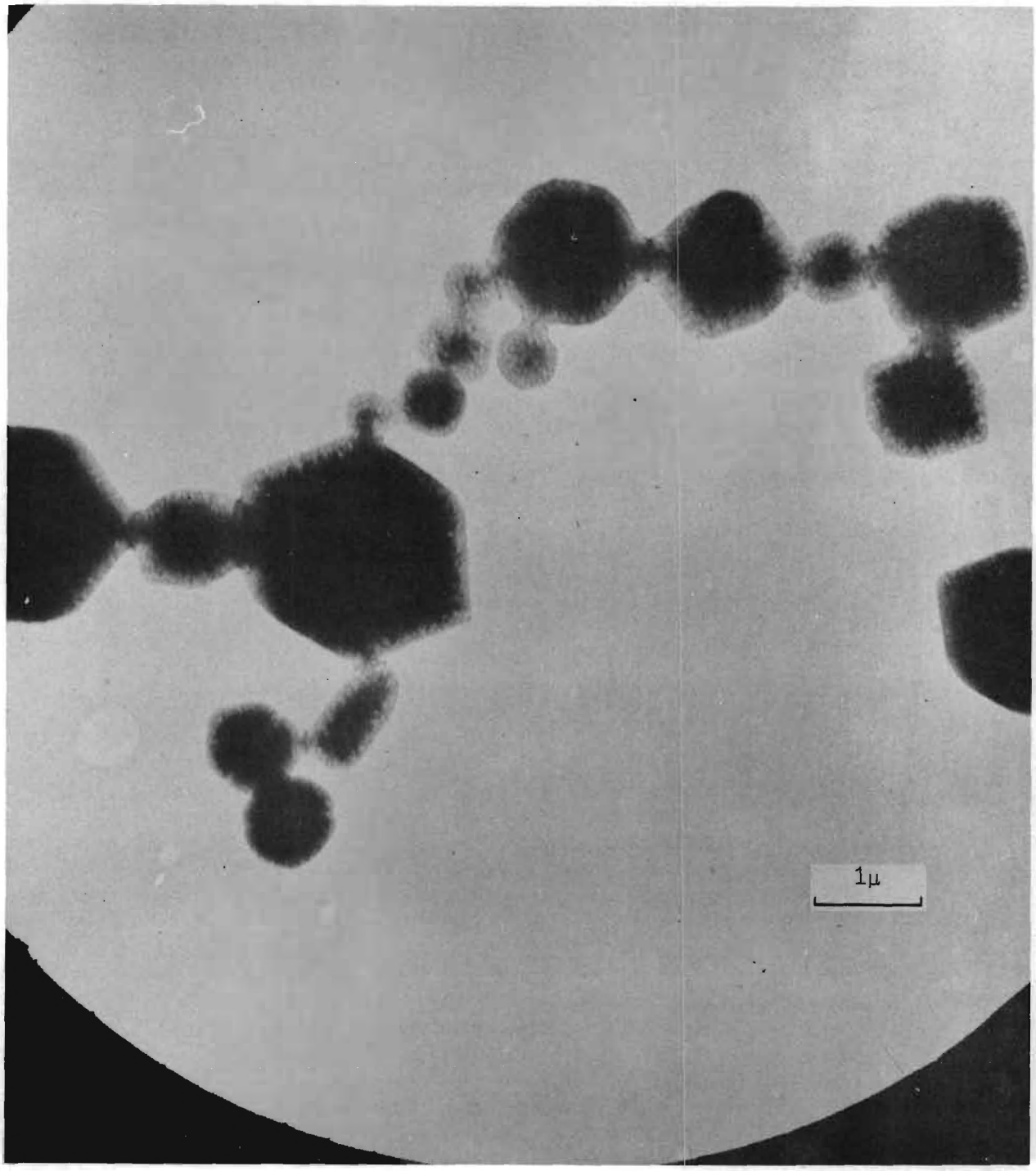

Figure 6. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

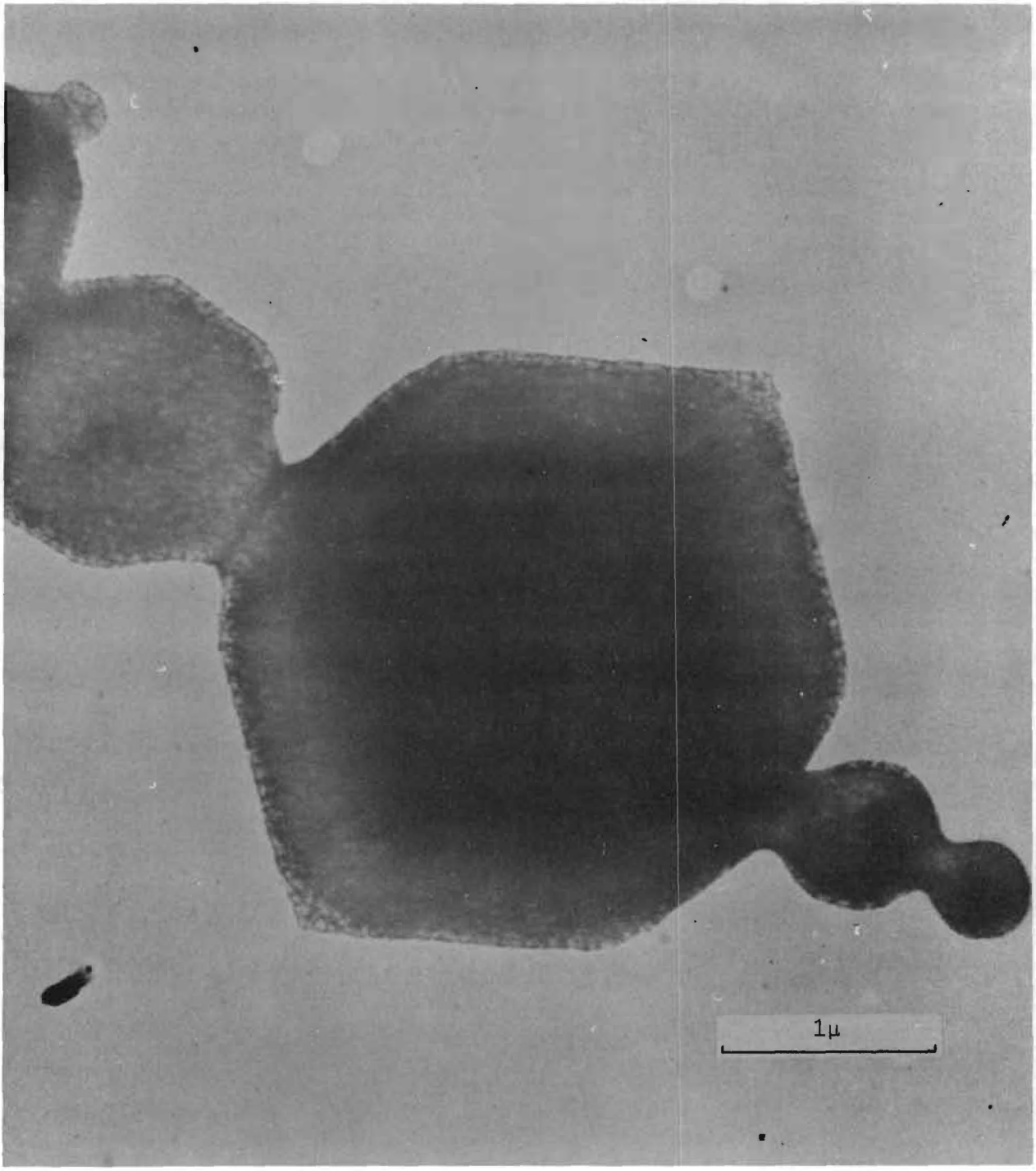

Figure 7. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

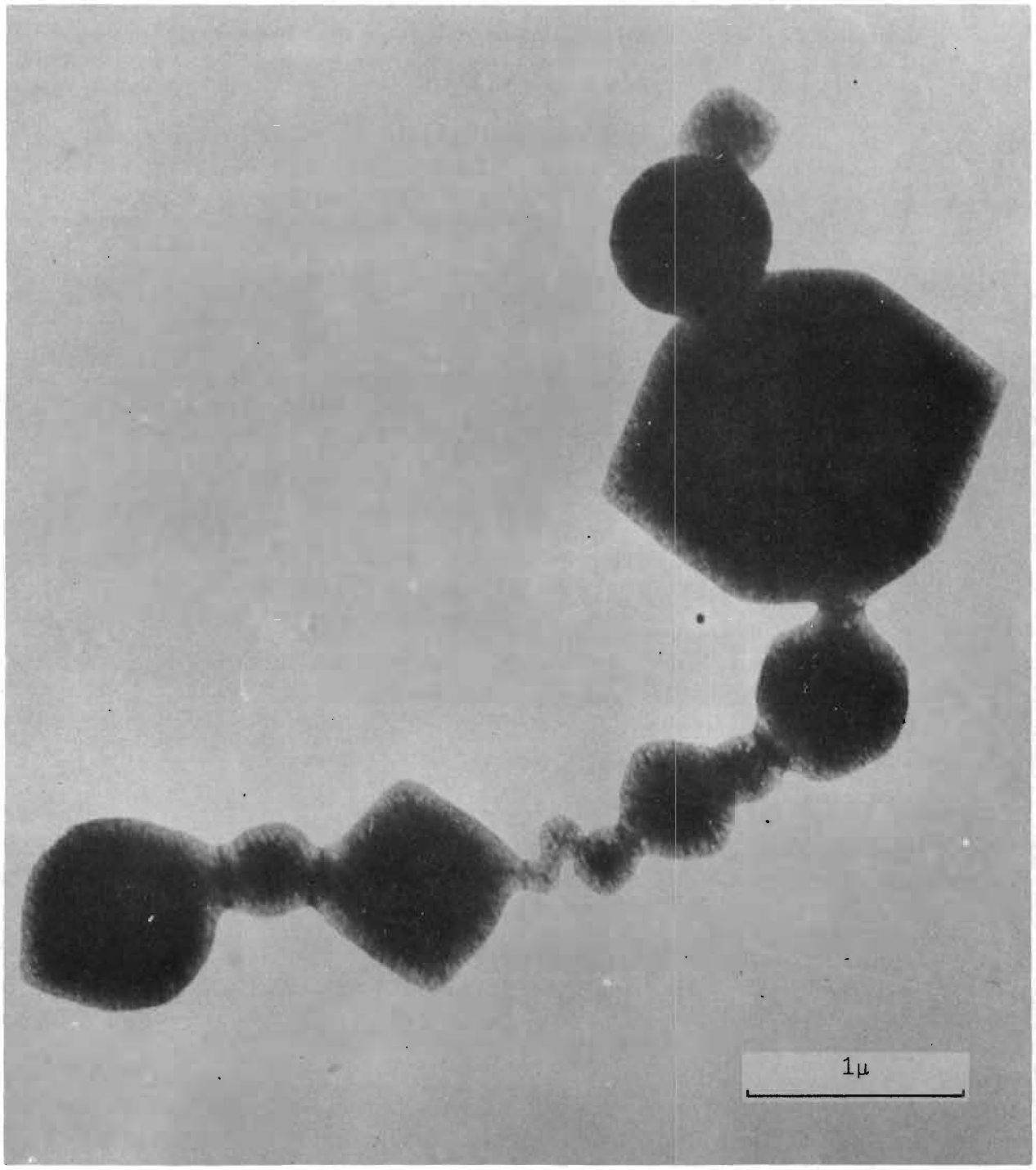

Figure 8. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

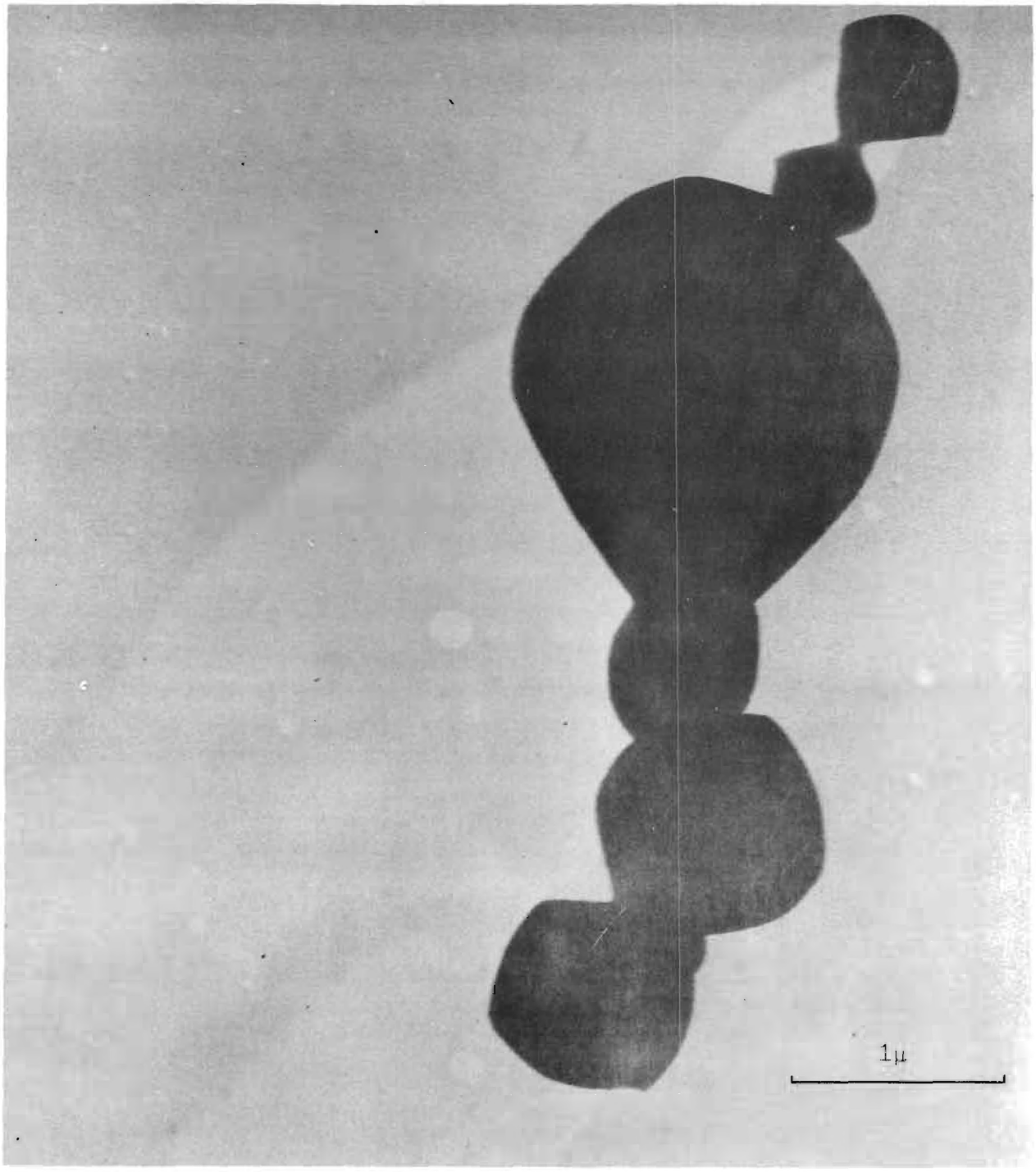

Figure 9. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration (Shadowed).

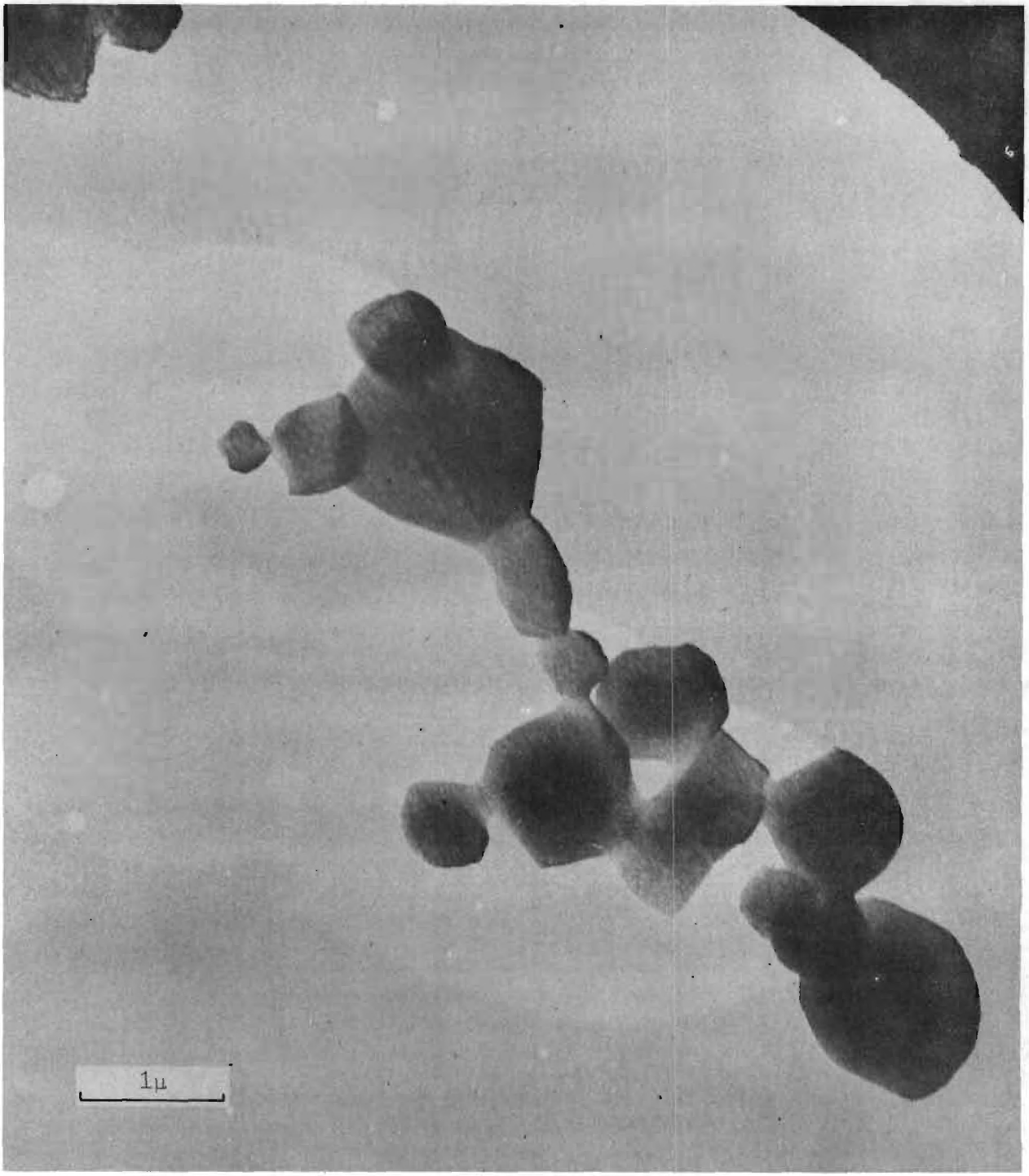

Figure 10. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration (Shadowed).

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
Atlanta, Georgia

FINAL REPORT

PROJECT NO. 161-101

INVESTIGATION OF AGGREGATION OF FINE PARTICLE MATTER SUSPENDED IN AIR

By

J. M. DALLAVALLE,
CLYDE ORR, JR., and L. A. WOODWARD

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CONTRACT NO. DA-18-064-CML-402

CHEMICAL CORPS - CAMP DETRICH

FREDERICK, MARYLAND

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JUNE 14, 1951

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
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(Continued)

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I. SUMMARY

Factors which affect the aggregation of aerosols were investigated. It was concluded that the electrical charge residing on ammonium chloride particles of the order of one-half micron in diameter (induced as a result of the generation of the particles or from the ions in the air) is of little importance in producing aggregation but does affect the chain-like orientation of the aggregated particles. The aggregative effect of naphthalene vapor was established and that of water vapor was investigated rather thoroughly. It was shown that at a relative humidity of 22 per cent or less no effect existed, while at 50 per cent, random agglomeration occurred. Between the two extremes chain-like aggregates, tending toward a more random arrangement as humidity increased, were found.

Methods for studying the effects of vapors have been established; the subject is believed worthy of additional study.

II. INTRODUCTION

The general objectives of this project were to study (1) the effects of the electrical charge of fine particulate matter suspended in air on the rate of aggregation of the individual particles, (2) the nature of the electrical charge, and (3) the nature of other cohesive factors affecting aggregation in an aerosol.

Despite a vast amount of work on many phases of aerosol behavior, comparatively few facts can be regarded as established. A number of investigators[6,*15,23,57,63,85,87] have described -- some in vivid detail -- the formation of chain-like aggregates of suspended particles. This suggests that the electrical character which the

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*Superscripts refer to the Bibliography in the Appendix.

particles possess may be responsible for this type of aggregation. Other investigators[3,5,11,15,26,27,28,37,40,47,50,85] have studied the relative amounts of the positively and negatively charged particles and the uncharged particles in an aerosol, the factors which produce or destroy the charge, and the total voltages present in a cloud of dust. Many of the questions raised by such investigations have not been answered.

An approach to the problem of electrical charge quite different from those used in any of the above mentioned investigations, and a phase of aerosol study that has been neglected in this country, was investigated in this work. Considerable work along similar lines was done in Europe, particularly Russia, a decade ago, however, many of the results are at variance. Consequently, efforts were directed toward a determination of the role of the suspending gaseous medium and the vapors that might be present therein. The primary means of analysis employed was the electron microscope, thus only qualitative data were obtained. However, significant facts were found which indicate serious need for additional qualitative studies and for an extension into quantitative data.

III. EXPERIMENTAL WORK

A. Equipment. The investigation used only well established techniques. The principal pieces of equipment employed were (1) a monodisperse aerosol generator, (2) a thermal precipitator, (3) an electron microscope, (4) an ultrasonic sound generator, (5) a shadowing apparatus, and (6) an aerosol chamber. Each apparatus is described in detail below.

(1) Aerosol generator: This apparatus was constructed in accordance with the detailed information given by Sinclair and La Mer[64] and was later modified to the extent that the nozzles directing the effluent from the boiler into the reboiler were lengthened so that the effluent was more likely to come into contact with the reboiler walls. The apparatus is shown in Figure 1.

(2) Thermal precipitator: The plans for this precipitator were furnished by Dr. Carlton E. Brown of the U. S. Army Chemical Corps. The apparatus was constructed in accordance with these plans with the exception that provisions for removing and replacing the sample screens were altered so that samples ready for immediate electron microscopic examination were obtained. The precipitator may be classed as a "moving-sample stationary-hot-wire" type. This type is generally recognized as superior to all others. It can be seen in the aerosol chamber in Figure 2.

(3) Electron microscope: An RCA type EMU electron microscope was used.

(4) Ultrasonic sound generator (Magnetostruction oscillator): The design developed by St. Clair[69] was followed. A picture of the apparatus is shown in Figure 3 of the Appendix and the circuit diagram is given in Figure 4.

(5) Shadowing apparatus: The metallic vapor shadowing apparatus shown in Figure 5 was used to obtain a three-dimensional effect in order to measure height, as well as length and width, of some precipitated aerosol samples.

(6) Aerosol chamber: A chamber approximately 20 inches along each edge was constructed from one-quarter inch thick polystyrene

sheets and fitted with a sealing door. It may be seen in Figures 1, 2, and 3. Polystyrene plastic was chosen for its favorable dielectric and moisture resistant properties.

B. Methods of Investigation. The production of alumina, silica, stearic acid, and ammonium chloride aerosols was investigated. The aerosols of alumina and silica were generated by mechanical dispersion of the respective powders with an elutriator,[12] the arrangement of which is shown in Figure 6, but it was impossible to obtain completely dispersed clouds by this means.

Aerosols of ammonium chloride produced by the direct mixing of ammonia and hydrochloric acid vapors were tested, but the corrosion caused by a slight excess of ammonia indicated that the use of another method would be preferable.

Generation (with the La Mer generator) of stearic acid aerosols of excellent monodisperse characteristics (judged by the intensity and brilliance of the colors from scattered light) was accomplished after optimum air flow rates, temperatures, and ion production rates were established. However, difficulties were encountered in collecting the stearic acid particles in the thermal precipitator without melting them. The slow evaporation of the particles during exposure to the vacuum existing in the electron microscope forced a search for another more suitable substance.

Subsequently, it was found that a satisfactory aerosol of ammonium chloride could be generated using solid ammonium chloride in the La Mer generator.

Ammonium chloride exhibits a propitious property; if an electron photomicrograph is taken without undue delay, the ammonium chloride

particles appear as black solids, but, after a few minutes exposure to the electron beam the particles become rather transparent, and a three-dimensional effect results. This is shown quite distinctly by the rather irregular and agglomerated particles of Figures 7 and 8. Ammonium chloride particles have been used in most of the work to date.

As mentioned above, the formation of chain-like aggregates is indicative of the presence of electrical charges. In order to produce aggregation at a relatively rapid rate so that the shape and characteristics of the aggregates might be studied, an ultrasonic generator was built. A sound generator was chosen for two reasons: first, agitation is produced without contact between the particles and any part of the generator such as would occur between a fan blade and the particles if a fan were used, and second, some work[52] indicated the existence of a minimum degree of agitation. Figures 9 through 12 show typical agglomerates resulting from sonic agitation.

In the literature [13,15,23,38,51,55,57,59,78] it has been noted that certain gases and vapors enhance aggregation, while others retard aggregation. A preliminary investigation of the effect of naphthalene vapor on a stirred aerosol of ammonium chloride actually showed some increase in the agglomeration, as can be seen by examining Figure 13. However, before the effect was thoroughly investigated with sonic agglomeration, it was found that water vapor produced a decided effect on the rate of agglomeration and this effect was carefully investigated.

C. Effect of Water Vapor. Ammonium chloride is a hygroscopic material. In the course of the investigation it was observed that, unless the ammonium chloride was heated at a temperature of more than

150° C. for from 12 to 24 hours, the aerosol produced was partially composed of particles with a crystalline structure. Such particles may be seen in Figure 14. However, by thorough drying of the ammonium chloride and by passing the air used in establishing the aerosol through a cascade of silica gel, calcium chloride, and anhydrous phosphorous pentoxide, an aerosol of spherical particles, such as those shown in Figures 15 and 16, was established.

The moisture content of the air was adjusted in the aerosol chamber, i. e., after an aerosol of spherical particles was established, by admitting moist air into the chamber. The moist air was produced by passing air through water-saturated gauze. The humidity of the chamber air was measured with a wet-dry bulb hygrometer at the exit from the chamber. The investigation presented several experimental difficulties. In order to measure the moisture content of the air, a certain minimum air flow rate must be maintained across the wet and dry bulbs of the thermometers of the hygrometer. In order to maintain this air flow rate through the chamber exhaust but not deplete the aerosol, the fresh aerosol and moist air must be fed into the chamber and an adjustment between these two inlet streams made so that constant aerosol concentration and exhaust rate will be maintained. The concentration was maintained at approximately 2×10^4 particles/cc., and the exhaust rate and timing of the experiments resulted in an ammonium chloride particle staying for an average time of approximately two hours in the chamber in each experiment.

Figures 15 through 24 show the results of the agglomeration of an ammonium chloride aerosol by the above treatment as the relative humidity was increased.

IV. RESULTS

The form of aggregates produced by ultrasonic vibrations is shown in Figures 9 through 12. Examination of these pictures (they were chosen as being representative) shows chain-like aggregates, which, in the case of short chains, are quite straight, with the particles diametrically aligned. Straight chains as long as one quarter of one inch, composed of hundreds of particles, have been observed, but such long chains are most often composed of straight segments only.

The aggregation produced in an ammonium chloride aerosol by 15 minutes' agitation by a small fan in the presence of naphthalene vapor is shown in Figure 13. The same agitation alone produced no aggregation. Phenol and alcohol vapors produced no detectable aggregation with the same agitation in a preliminary investigation.

The aggregative effect of water vapor may be partially explained by the series of photomicrographs, Figures 14 through 24. Below a relative humidity of 22 per cent no aggregation resulted. At a relative humidity of about 50 per cent, completely unoriented aggregation occurred, probably as a result of random collisions, the particles being cemented together as a result of a partially dissolved film on their surfaces. At intermediate humidities the preferred orientation as a straight chain was evident, and observation of a great number of samples has convinced the investigators that the high proportion of such chain-like aggregates to the apparently unorientated aggregates cannot be the result of completely random collisions. At high humidities, at least, one would expect moisture in the air and on the particle itself to cause neutralization of electrical charge. At lower humidities, however, it may be that a diametrically opposed

charge is produced by the water vapor. The work of Gwathmey and associates[20,21,22] on single spherical crystals of metals indicates that certain areas on a crystal surface are many times more active than others, but to say these effects exist in the case of ammonium chloride must be regarded as pure speculation at this time. The reverse may even be true; the absorbed water vapor may cause the electrical charge (if the particles are originally uniformly charged) to be dissipated in spots at low humidities and over the entire surface at high humidities.

The present state of knowledge of aerosol aggregation is given in the Appendix, pages 10 through 12. A bibliography of many of the most important and recent literature contributions is also included in the Appendix.

V. CONCLUSIONS

Thus far, the studies indicate that as a result of the short range of the electrical force residing on ordinary aerosol particles, the primary influence of the charge is the orientation of the particles brought into proximity by forces such as Brownian and thermal motion.

Certain vapors cause pronounced changes in the aggregation of aerosol particles, probably through the mechanisms of altering the charge and charge distribution of a particle and by acting as a cementing agent.

The effects of vapors and charged or polarized aerosols on other aerosols should receive additional study.

Respectfully submitted,

J. M. DallaValle,
Project Director

Clyde Orr, Jr.,
Research Assistant

L. A. Woodward,
Research Associate

Approved

Gerald A. Rosselot, Director
State Engineering Experiment Station

VI. APPENDIX

THEORY OF AGGREGATION

The theory of aggregation of monodisperse systems has been worked out by von Smoluchowski[66] who derived the expression for the concentration

$$n = \frac{n_o}{1 + 4\pi D R n_o t} , \qquad (1)$$

where n = concentration at any time,

n_o = initial concentration,

D = the diffusiom coefficient,

R = the "active" radius of the particles involved, and

t = time.

The development given by von Smoluchowski requires that, once coalescence takes place between two particles, a third, fourth, etc. particle coalescing with them must have no tendency to separate. Equation (1) can be put into the form

$$- \frac{dn}{dt} = 4\pi D R n^2 = K n^2 , \qquad (2)$$

where K can be called the coefficient of coalescence. Equation (2) has been tested by Whytlay-Gray and collaborators[87] and found to represent certain experimental data.

An almost analogous expression has been obtained by Tunitskiĭ[27] relative to the decrease in the amount of charge on a monodisperse system as coalescence takes place. If Z is the charge at time t,

$$Z = \frac{Z_o}{1 + 1/2 K n_o t} , \qquad (3)$$

where Z_o = total initial charge,

and the other symbols are as before. This is derived on the assumption that the charge on each particle is the same at time $t = 0$. Tunitskiĭ

also gives the distribution of charges of particles of size x as

$$F(Z,x) = \frac{2\,b\,x\,Z}{e^{2bxZ} - 1}\ , \qquad (4)$$

where $b = \epsilon^2/4rkT$,

x = particle size at any time,

r = initial particle size,

ϵ = the value of the fundamental charge,

k = Boltzmann's constant, and

T = absolute temperature.

No expression has been derived either for coalescence or charge when the initial distribution is polydisperse.

It does not appear from these investigations that electrical charge is important in causing particle aggregation. Results show that, even at relatively high concentrations, monodisperse systems persist after long periods of time. The particles of stearic acid (almost 0.75 microns in diameter) and ammonium chloride showed little tendency to aggregate unless they were violently agitated or were influenced by certain organic vapors. The probability that all the charged particles were of like charge must be considered in relation to the persistence of dispersion. It is well established that the effect of electrical charge does not extend very far beyond the surface of a particle (inverse square law), and there is reason to suppose that Brownian motion and thermal turbulence are of greater importance in so far as aggregation is concerned.

As an example of the requirements for aggregation of particles, assume that the effect of an electrostatic field does not extend much beyond three particle diameters if aggregation is to take place. Then, if the particles have a diameter of one micron and an initial concentra-

tion of the order of 10^9 particles per cc., a mean distance between each of about 5.5 microns is required before the electrostatic forces are effective. Such concentrations are so dense that aggregation by direct contact due to thermal turbulence is more probable.

Concerning the forces that hold the particles together once they have come into contact with others, the surface energy theory of Bradley[8] and the theory of Beischer[6], which considers van der Waals' forces, surface diffusion and electric forces, are of interest. Bradley considers that the nature of the binding force is one of surface energy. He finds that the surface energy, σ, is of the order of 10^{-4} dynes per cm.[2] Thus, for particles of one micron in diameter, the binding force is

$$F = 2\pi r\sigma = 2\pi \times 1/2 \times 10^{-4} \times 10^{-4}$$
$$= 3.1 \times 10^{-8} \text{ dynes.}$$

The general expression for the binding force as obtained by Bradley is

$$F = \frac{4\pi r_1 r_2}{r_1 + r_2} \cdot \sigma \qquad (5)$$

where the r's are the radii of the particles aggregating, indicating that the forces are greater when one of the particles is smaller than the other. Thus, once aggregation has started, additional particles will be bound more tightly. In other words, the aggregated areosol is more stable as the individual particles increase in size.

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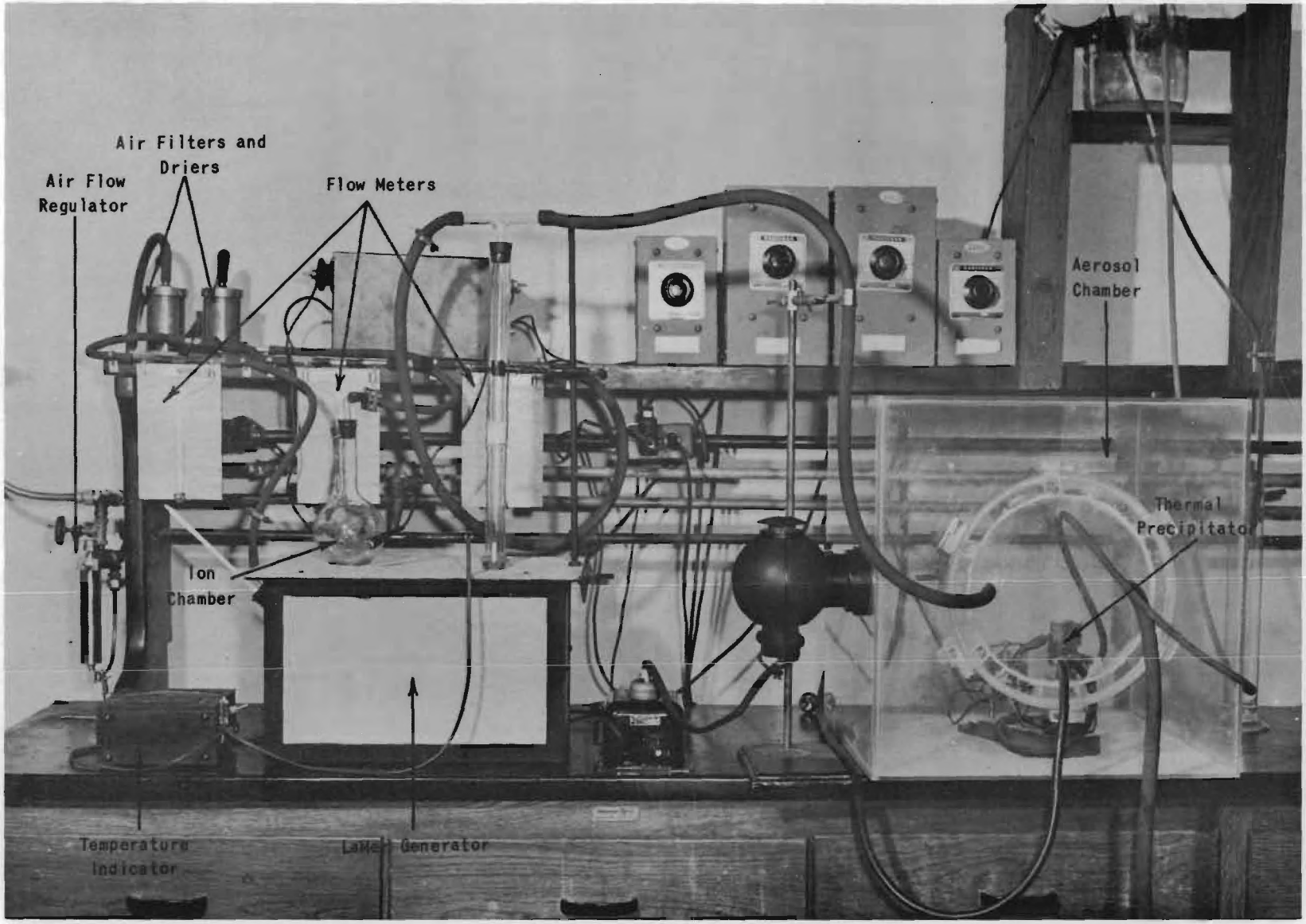


Figure 1. La Mer Aerosol Generator and Aerosol Chamber.

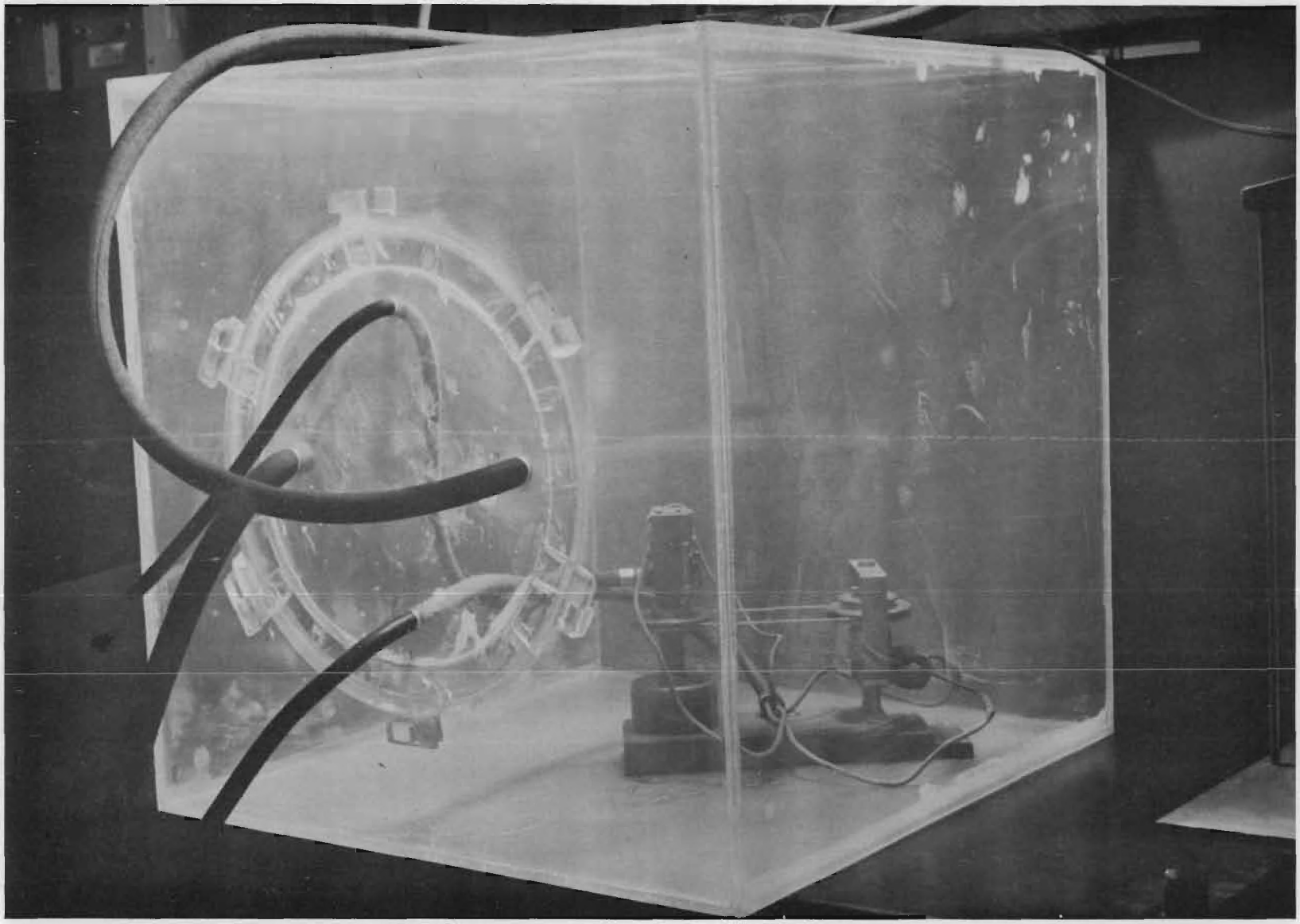


Figure 2. Thermal Precipitator in Aerosol Chamber.

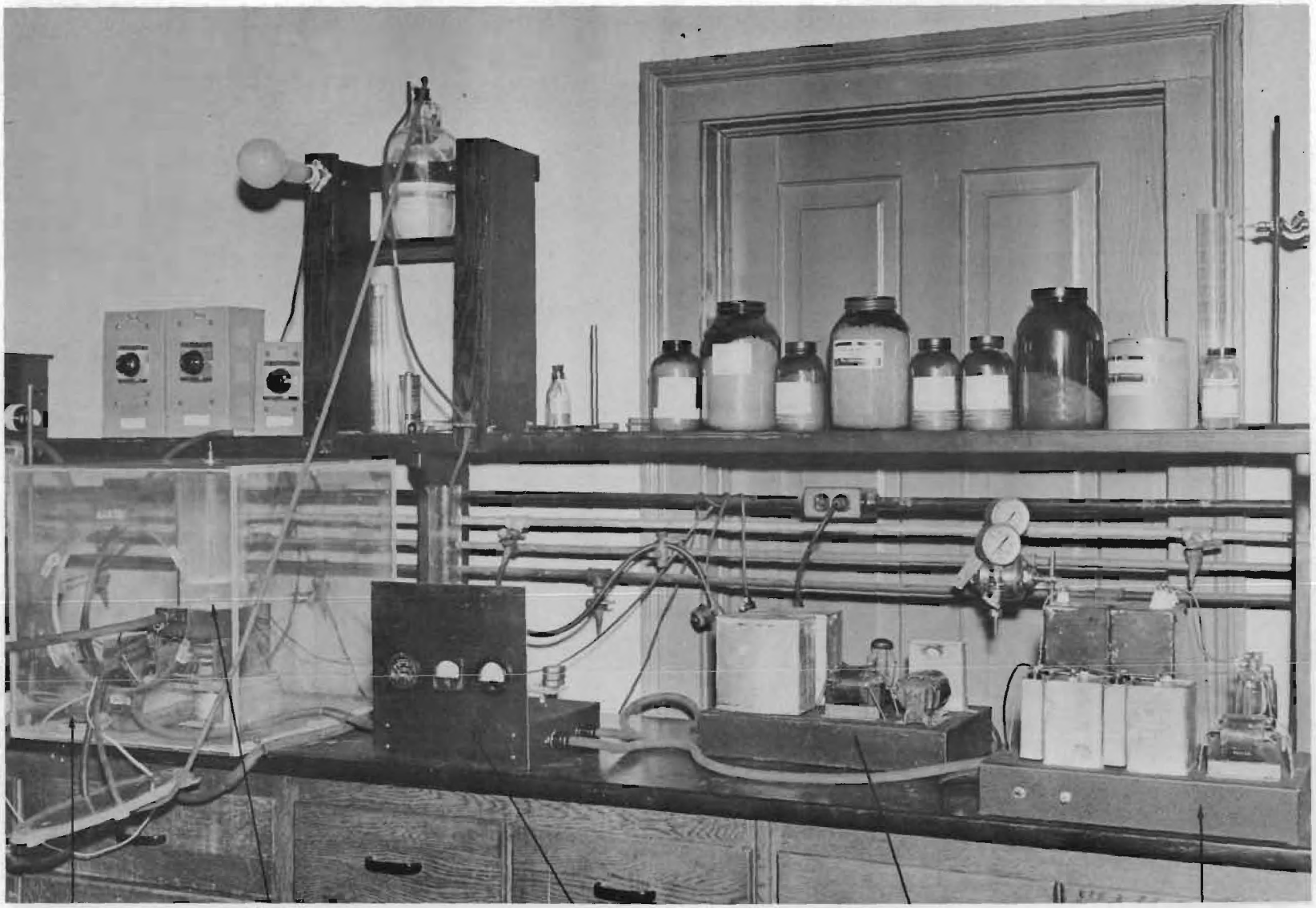


Figure 3. Magnetostriction Oscillator and Aerosol Chamber.

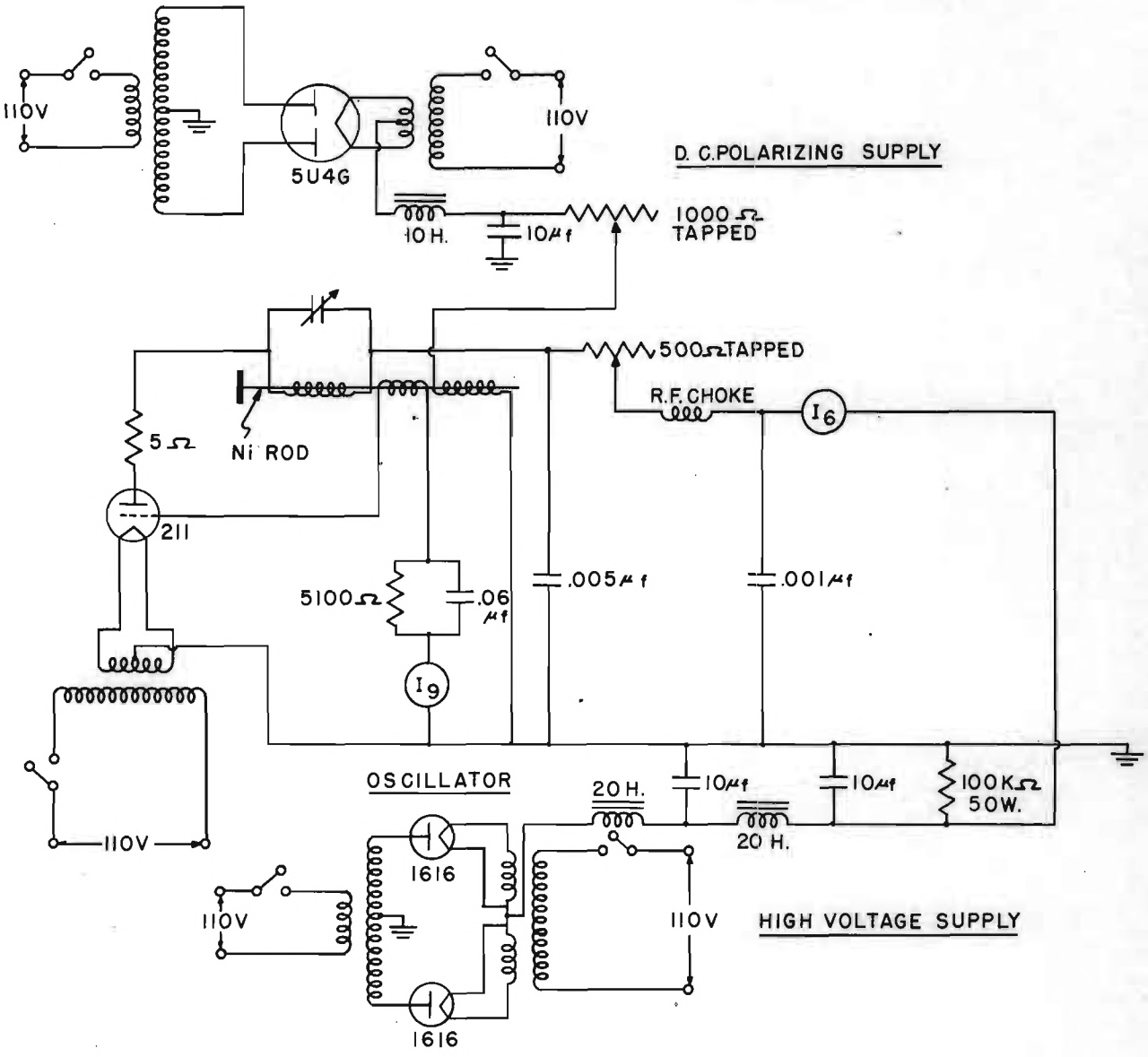


Figure 4. Magnetostriction Oscillator and Circuit Diagram.

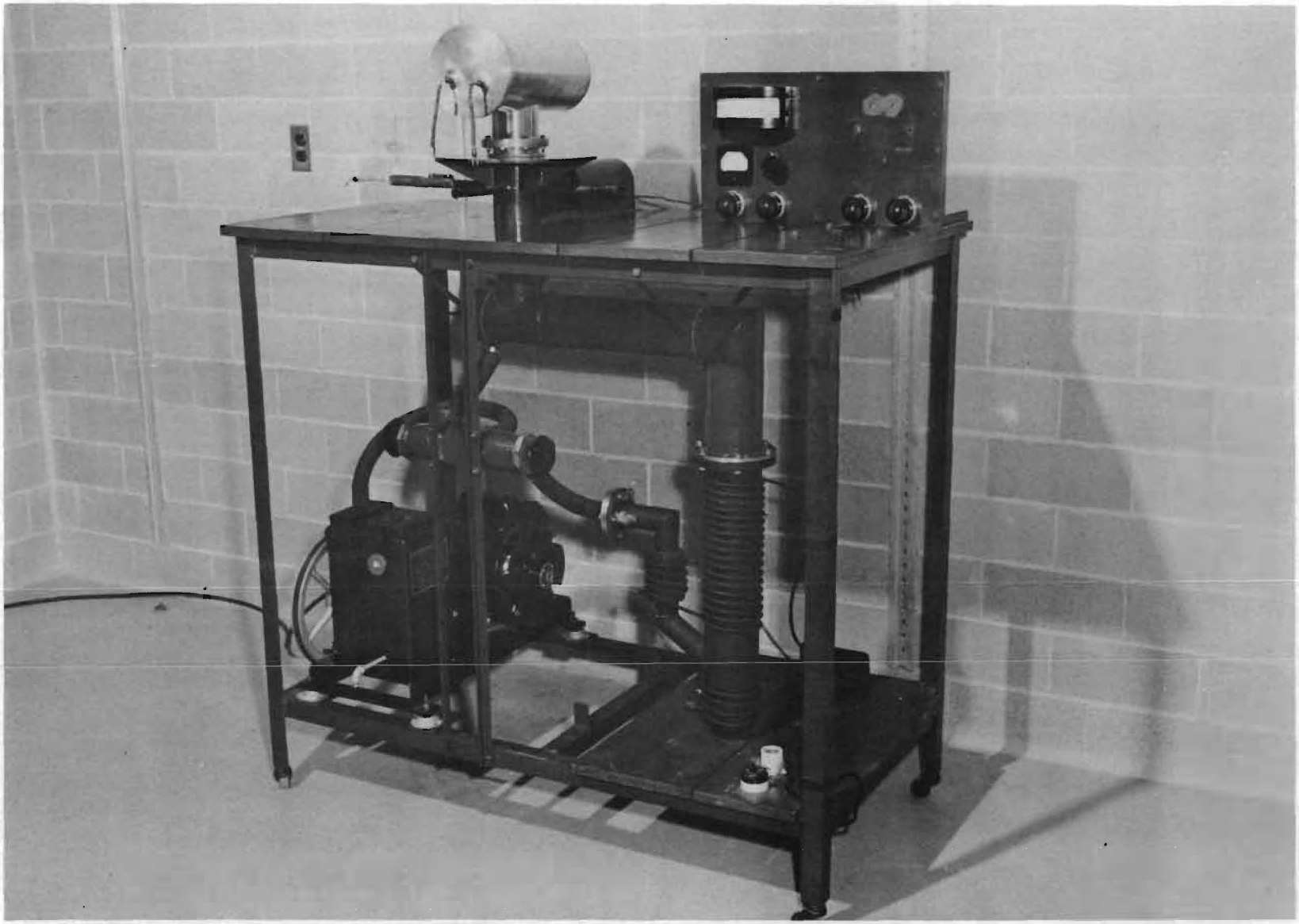


Figure 5. Shadowing Apparatus.

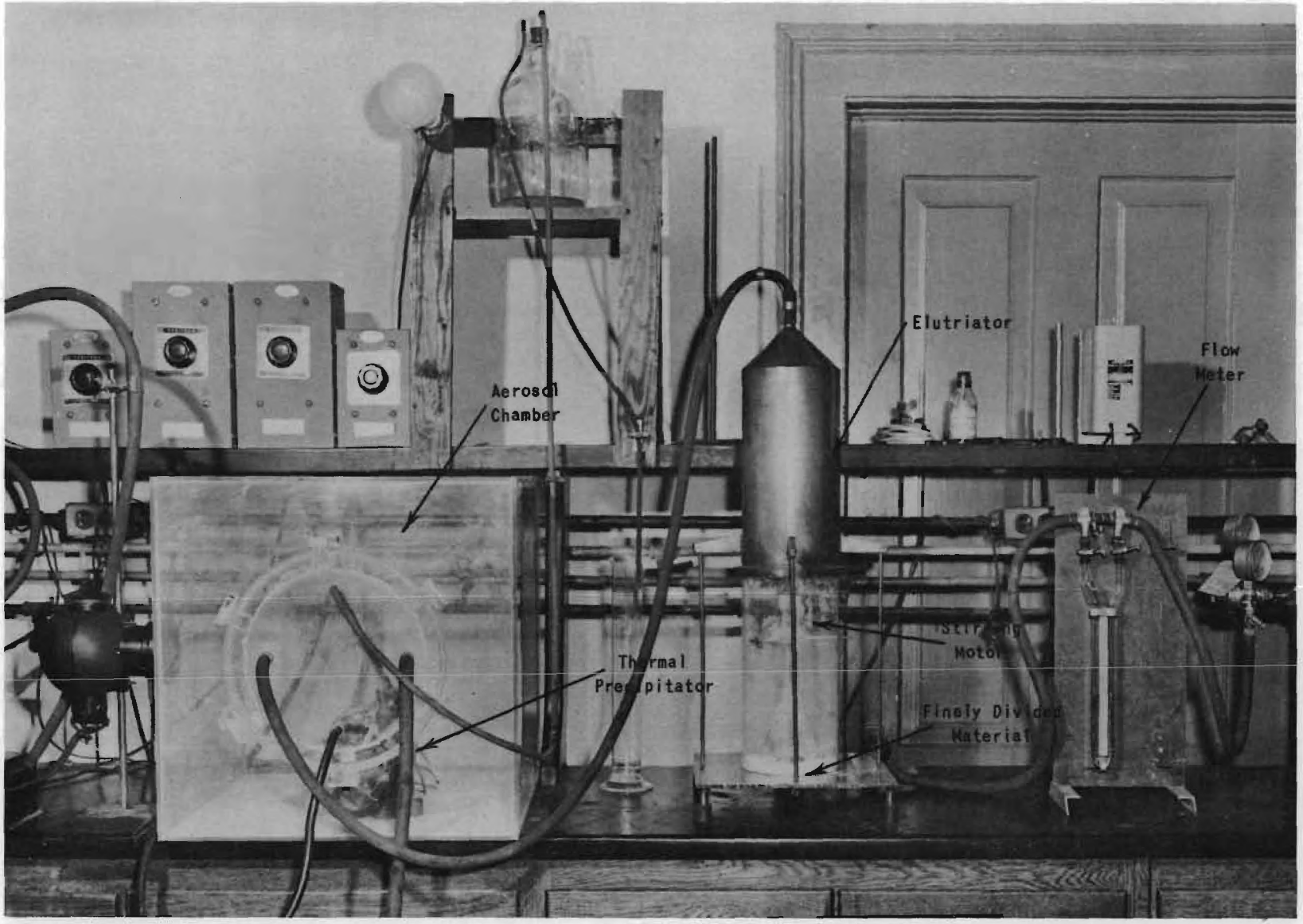


Figure 6. Elutriator Arrangement for the Generation of Aerosols.

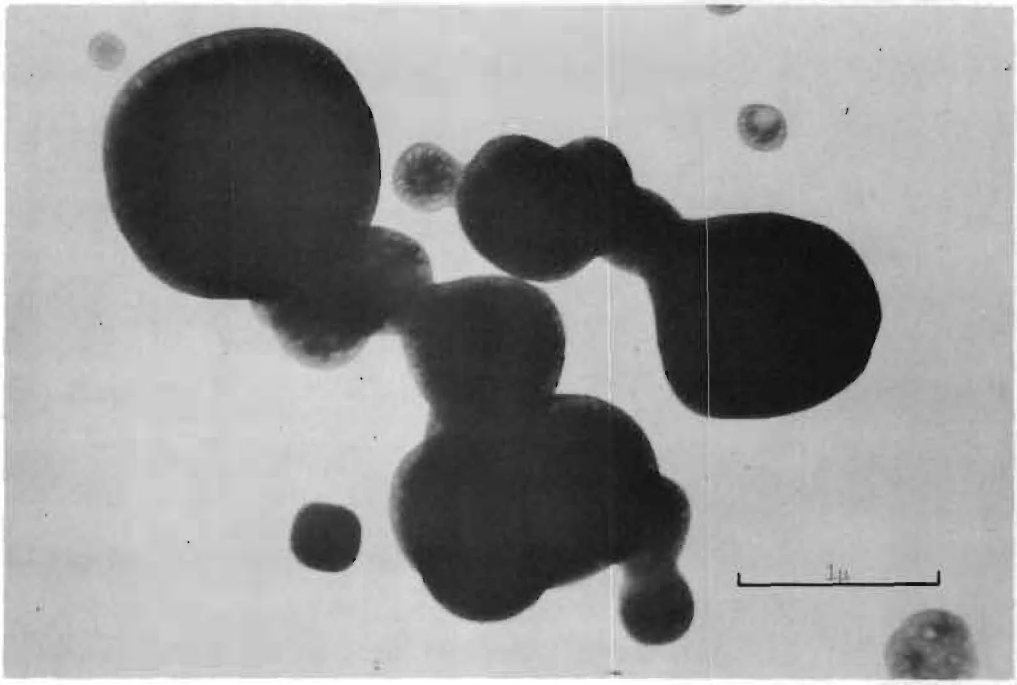


Figure 7. Ammonium Chloride Particles after a Brief Exposure to the Electron Beam of an Electron Microscope.

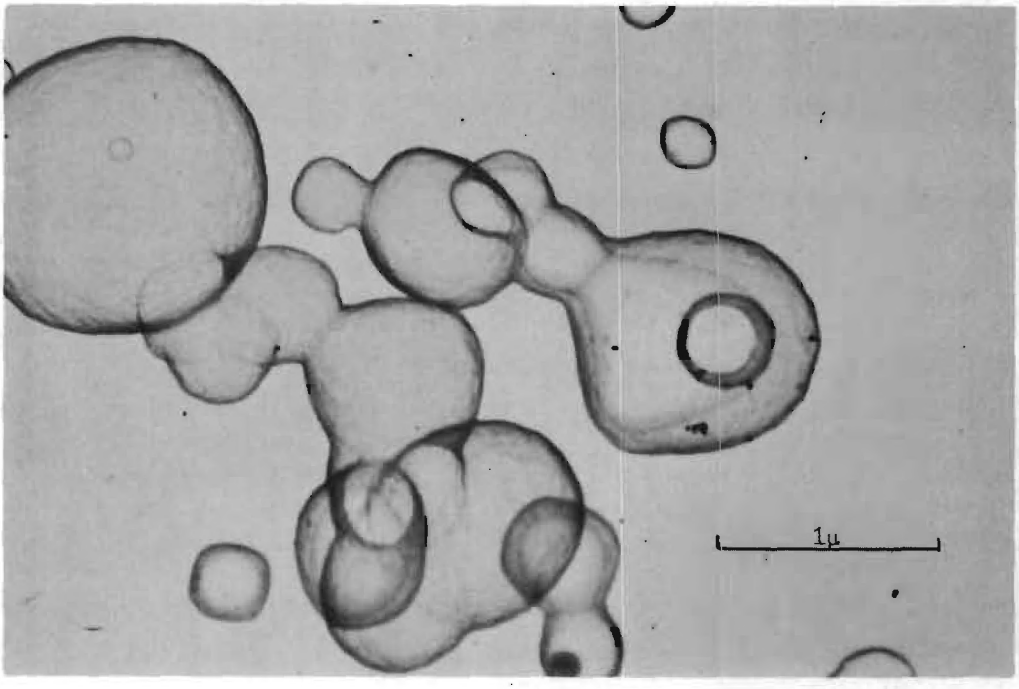


Figure 8. Ammonium Chloride Particles after a Three-Minute Exposure to the Electron Beam of an Electron Microscope.

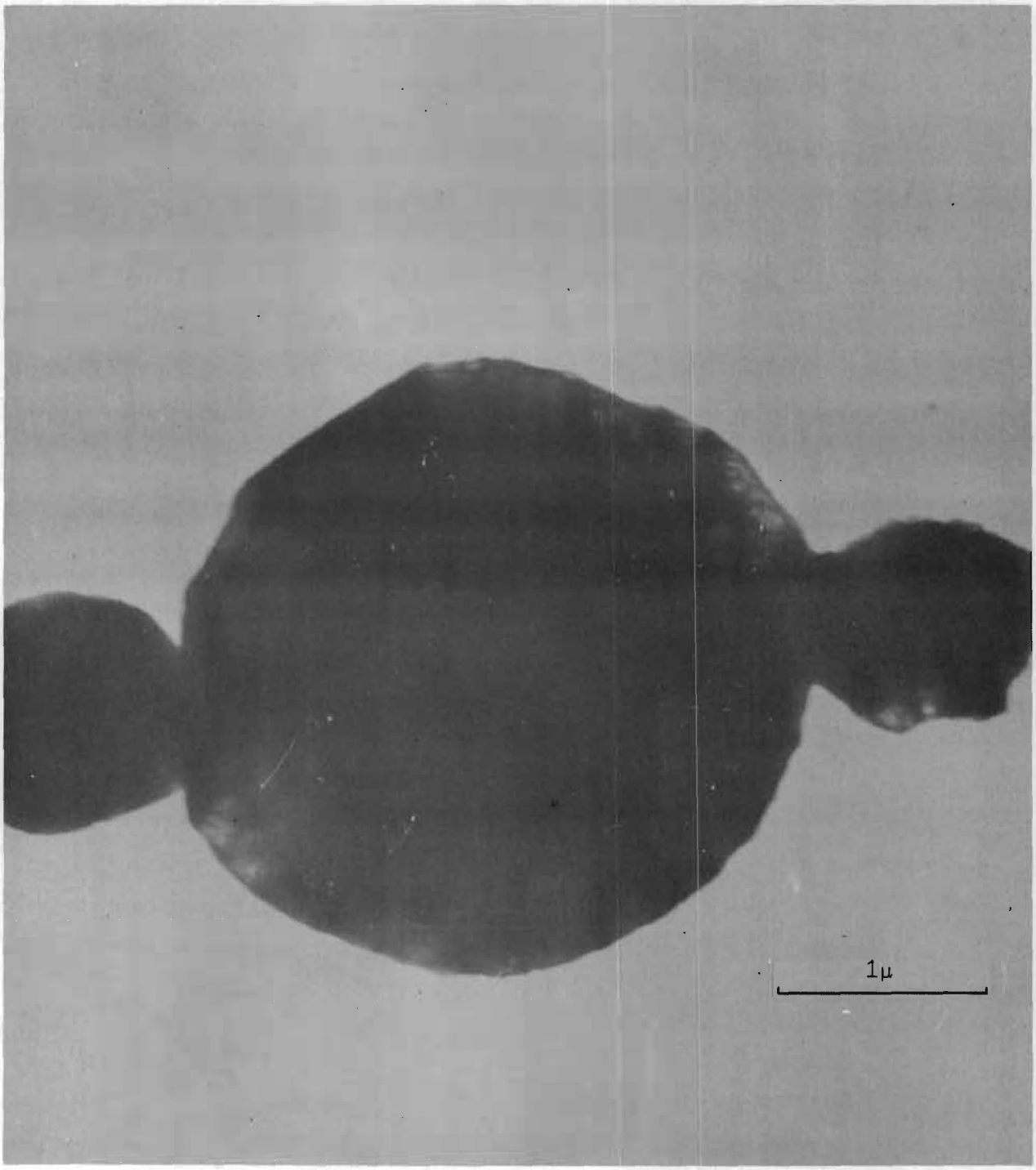


Figure 9. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

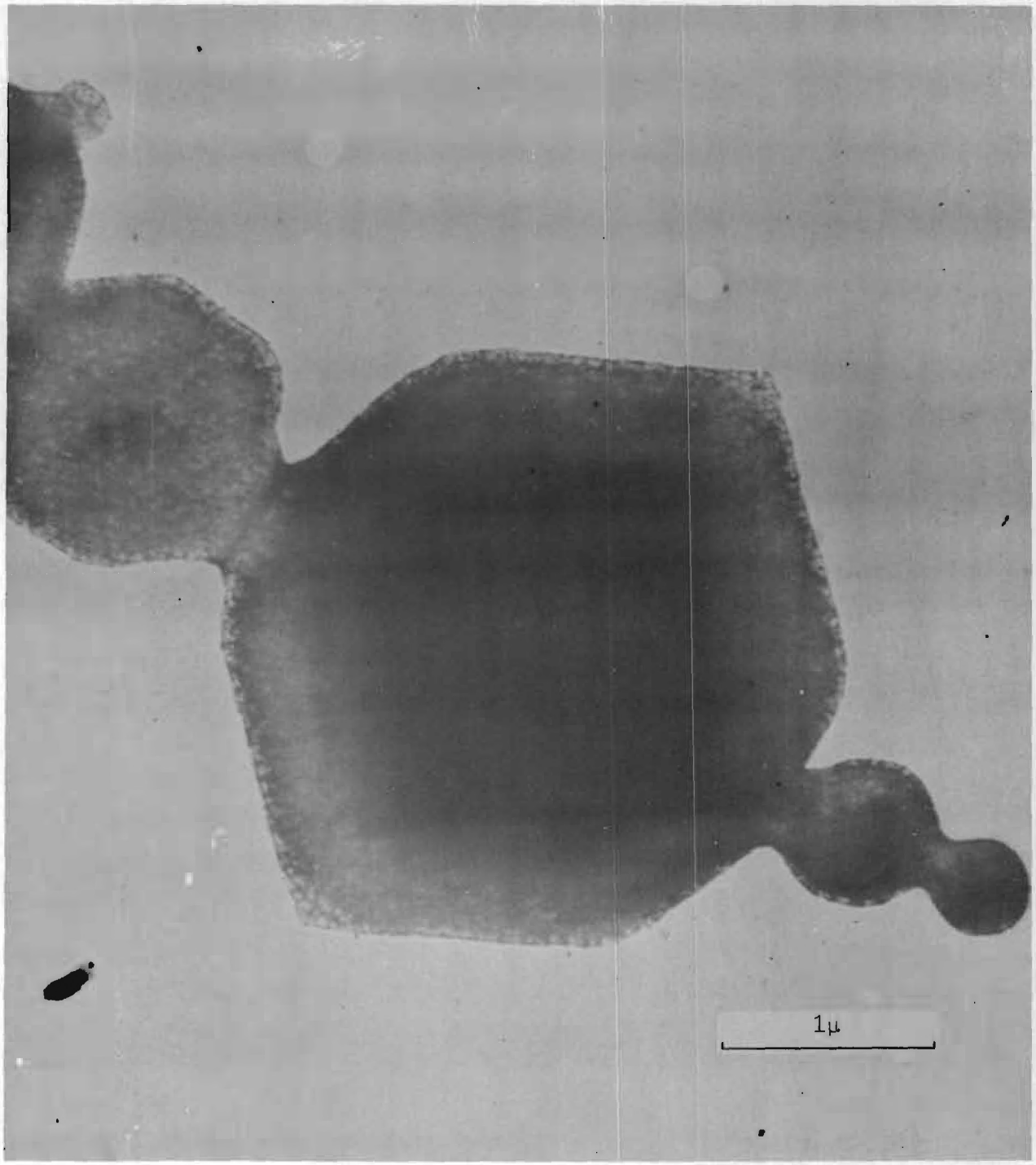


Figure 10. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

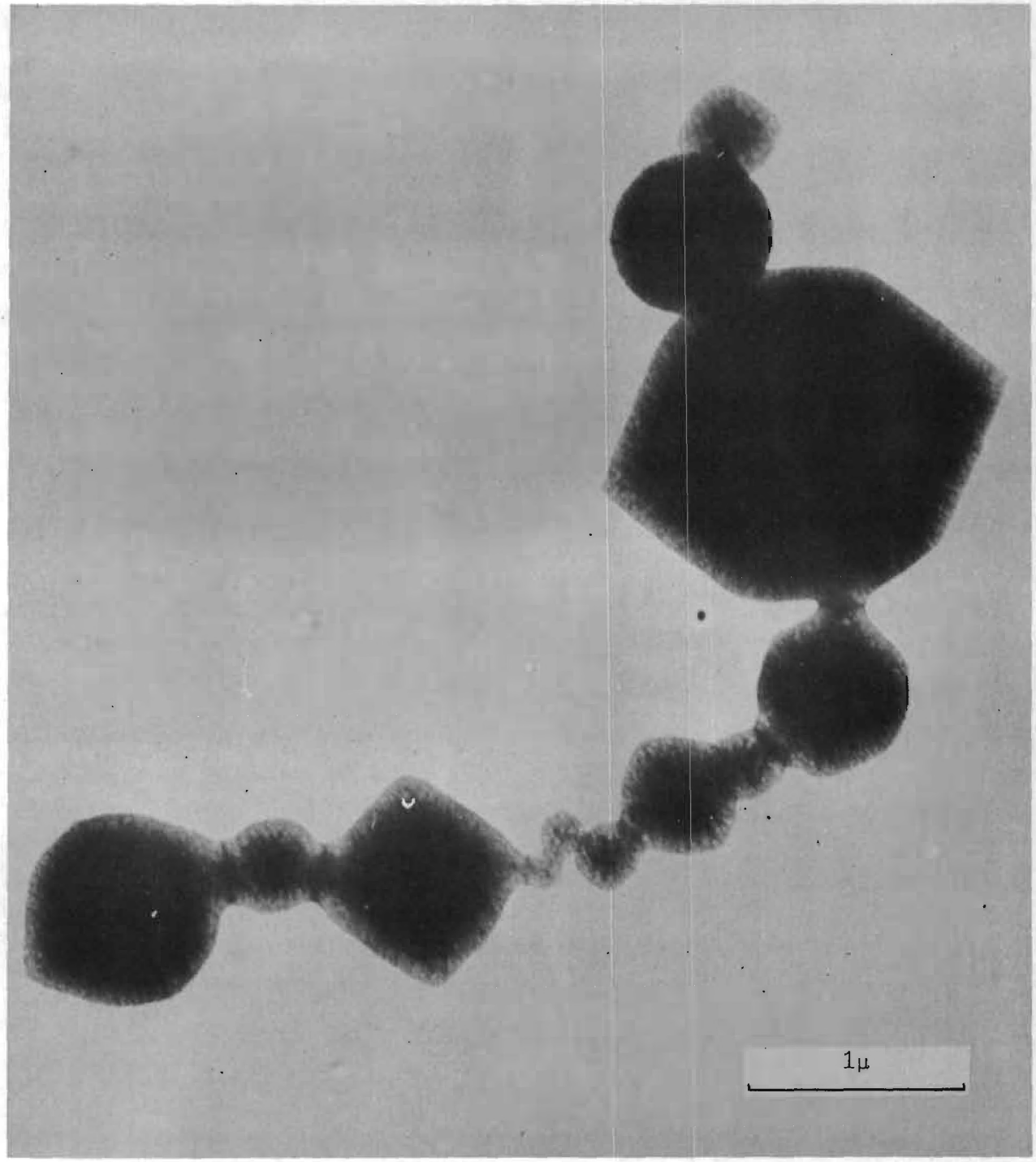


Figure 11. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration.

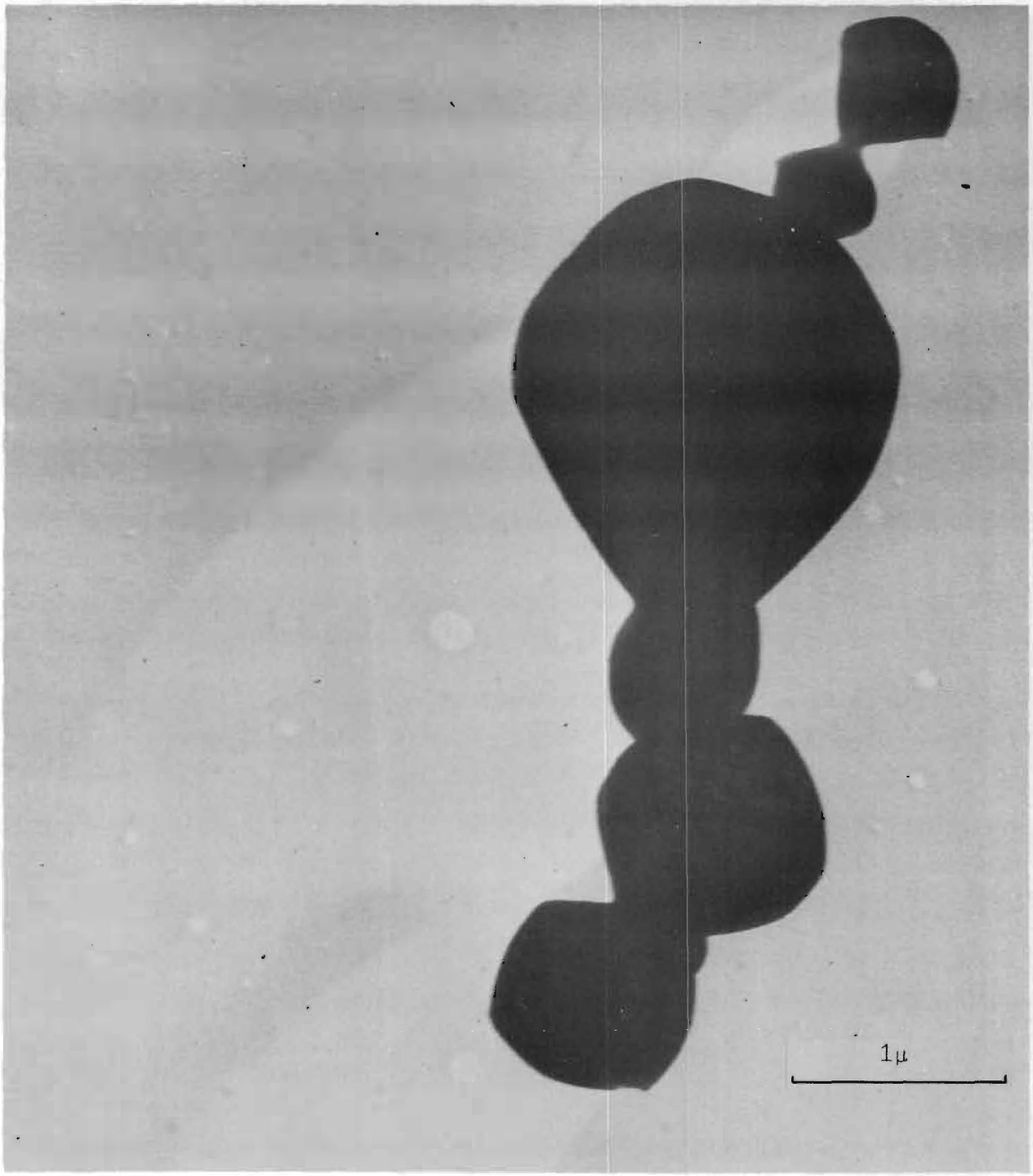


Figure 12. Ammonium Chloride Particles Aggregated by Ultrasonic Vibration (Shadowed).

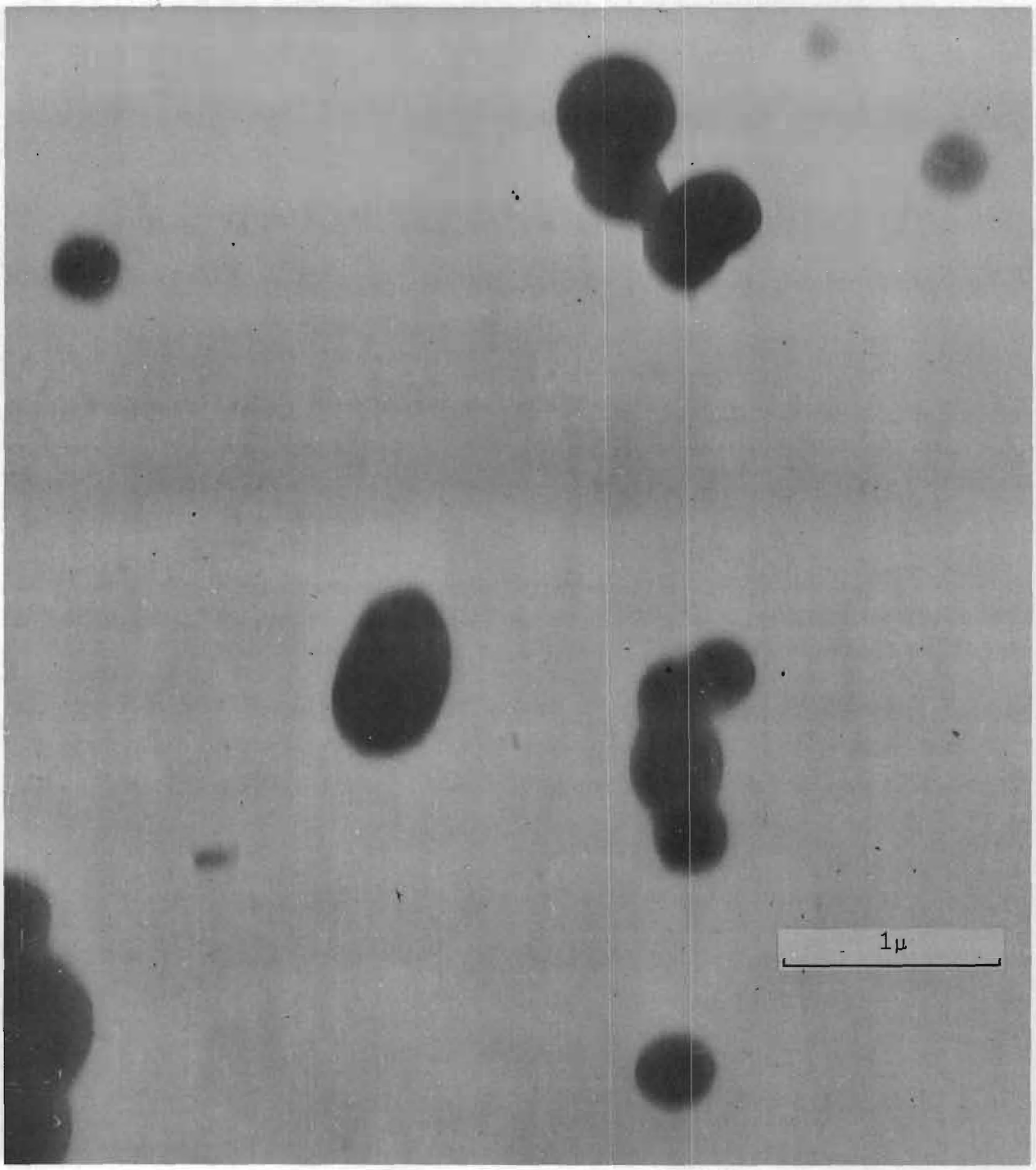


Figure 13. Ammonium Chloride Particles Aggregated by Naphthalene Vapor.

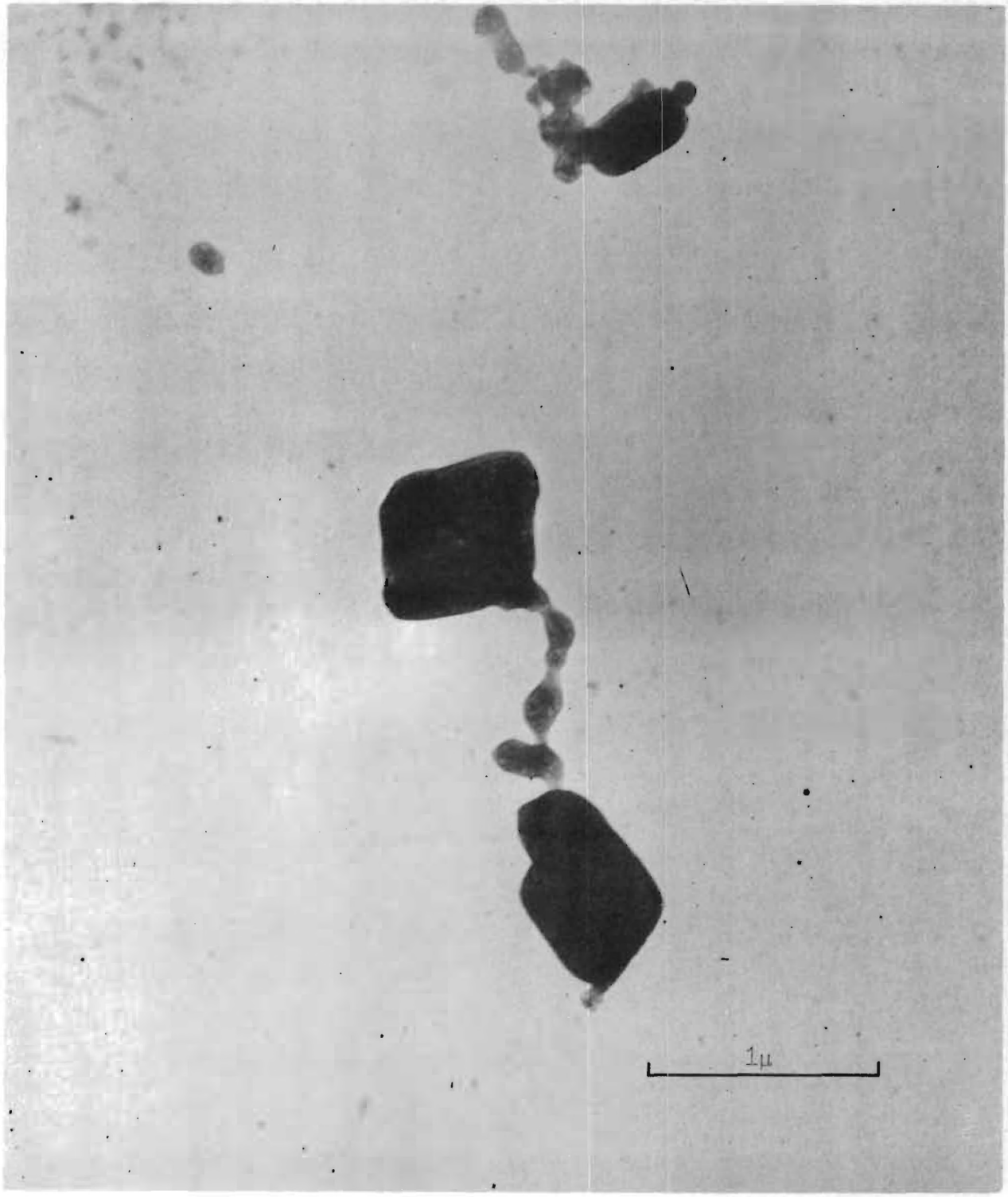


Figure 14. Ammonium Chloride Particles Generated from A Moist Sample.

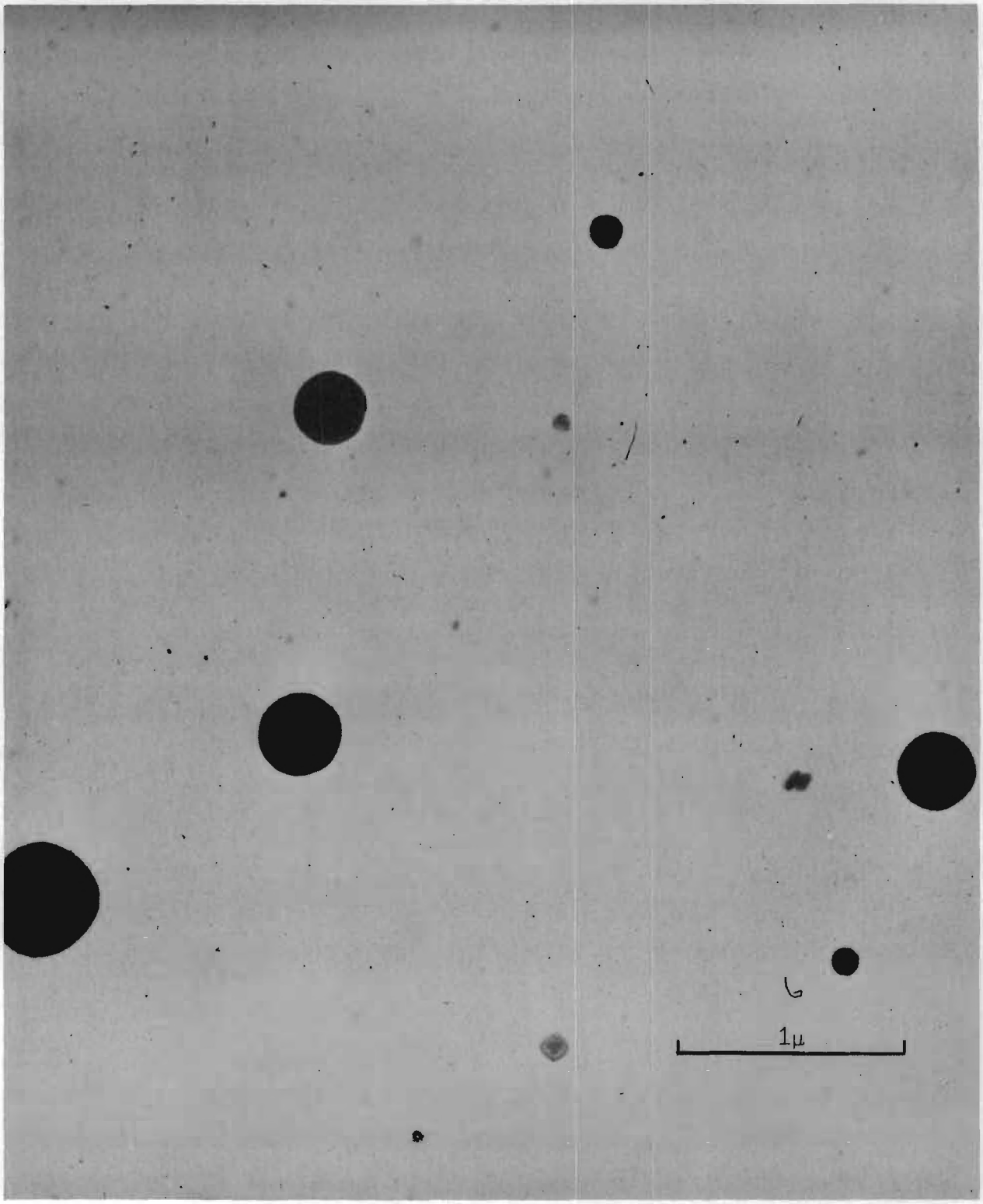


Figure 15. Ammonium Chloride Particles Exposed to Air of 22 Per Cent Relative Humidity.

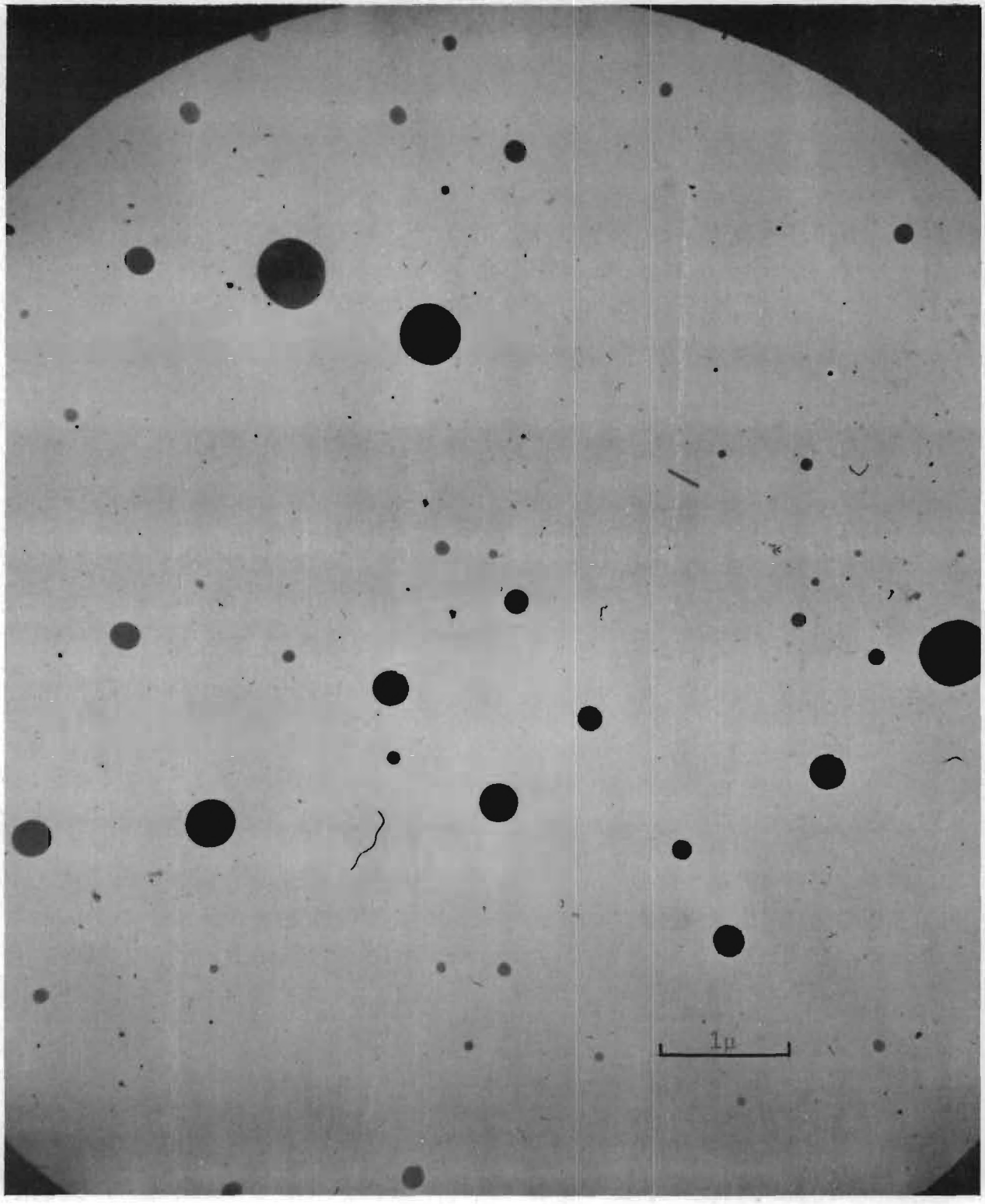


Figure 16. Ammonium Chloride Particles Exposed to Air of 22 Per Cent Relative Humidity.

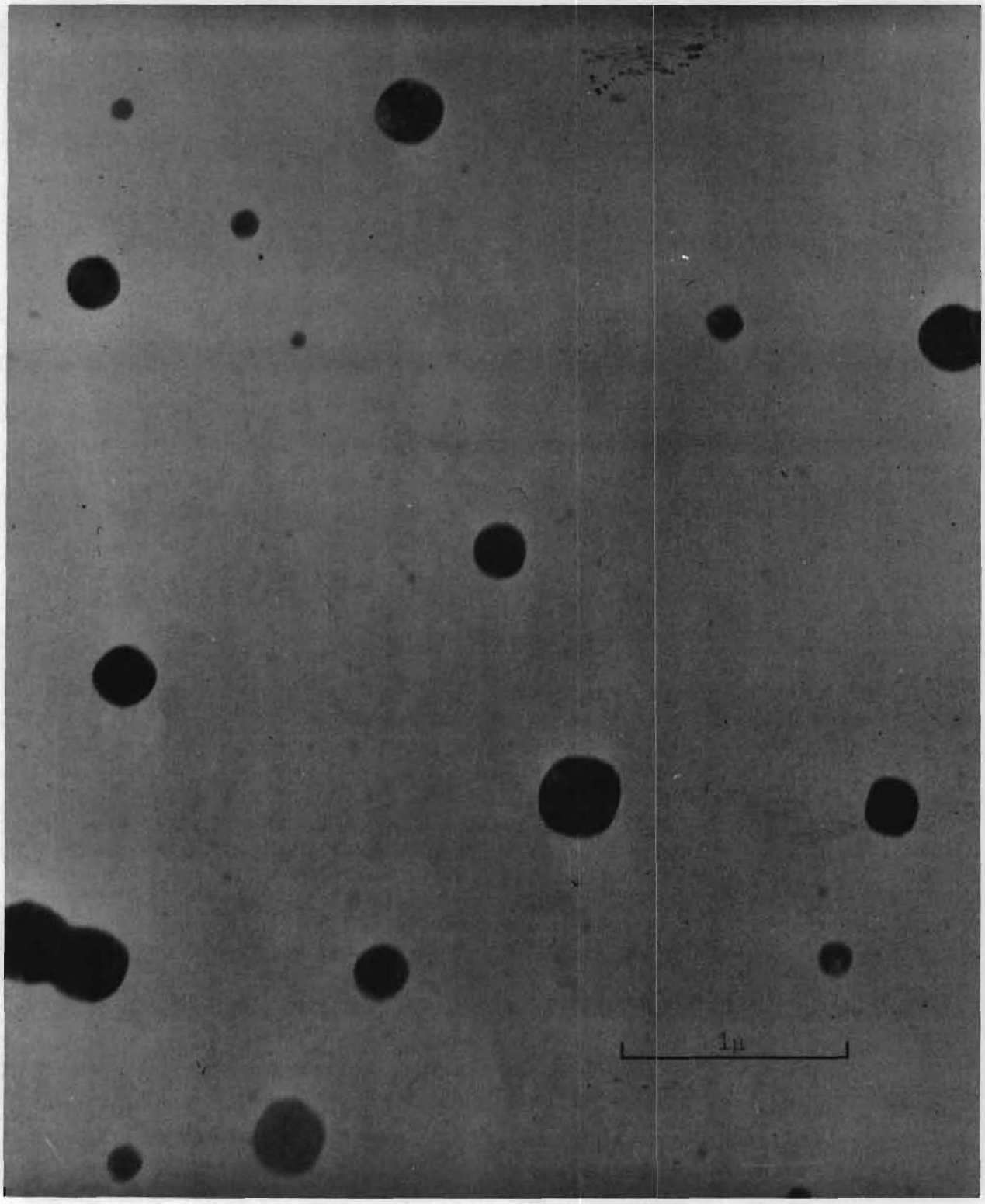


Figure 17. Ammonium Chloride Particles Exposed to Air of 30 Per Cent Relative Humidity.

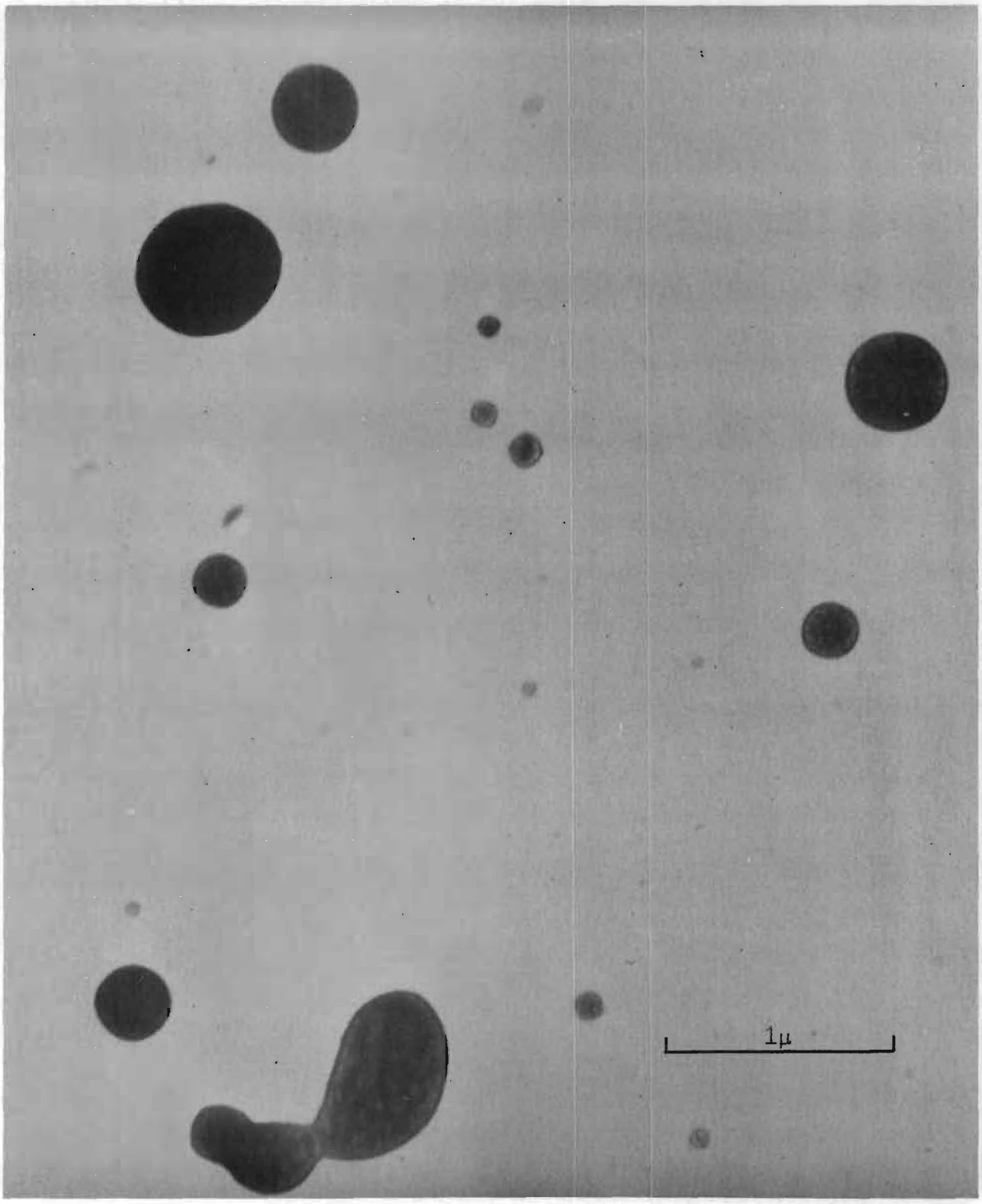
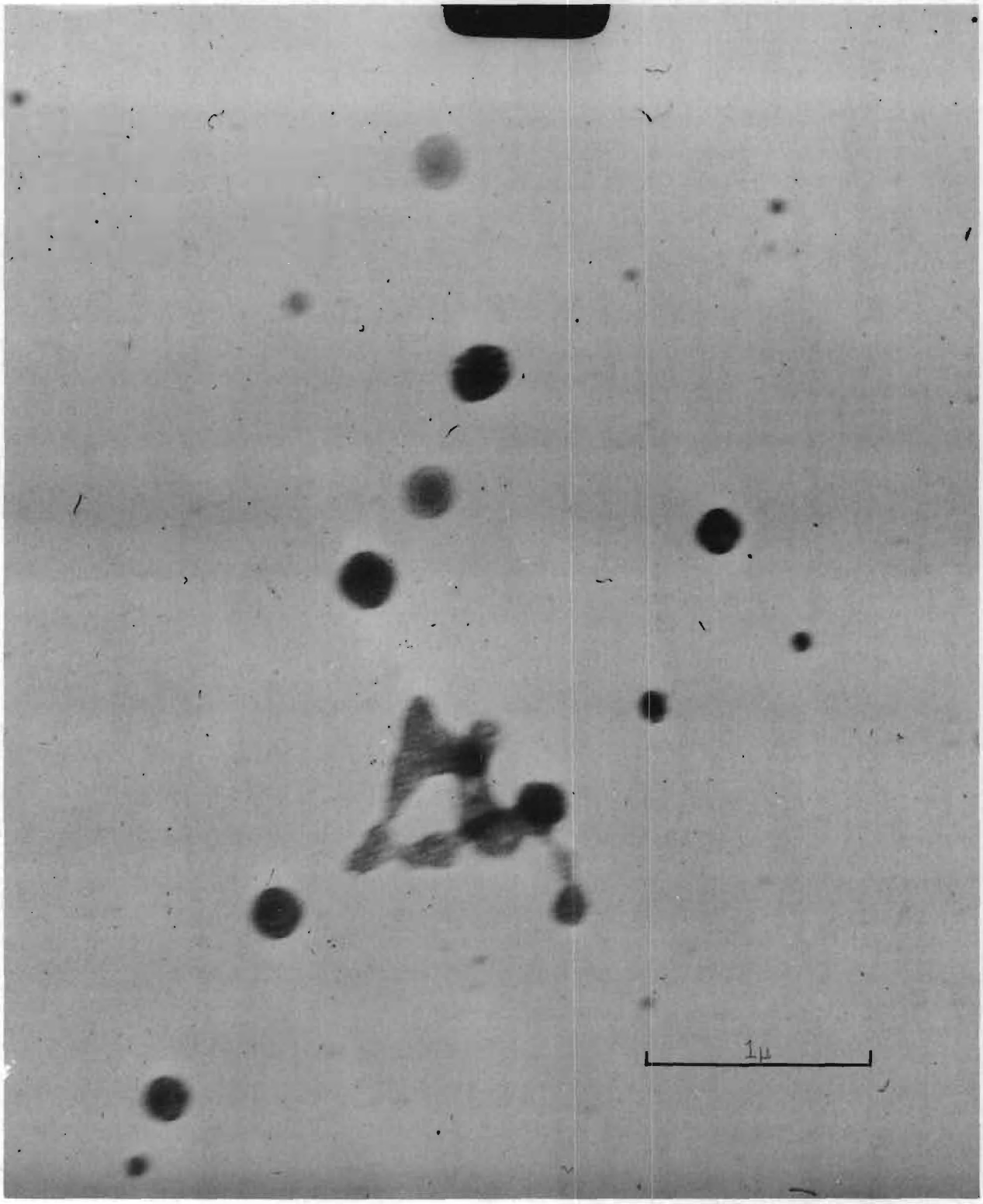


Figure 18. Ammonium Chloride Particles Exposed to Air of 30 Per Cent Relative Humidity.



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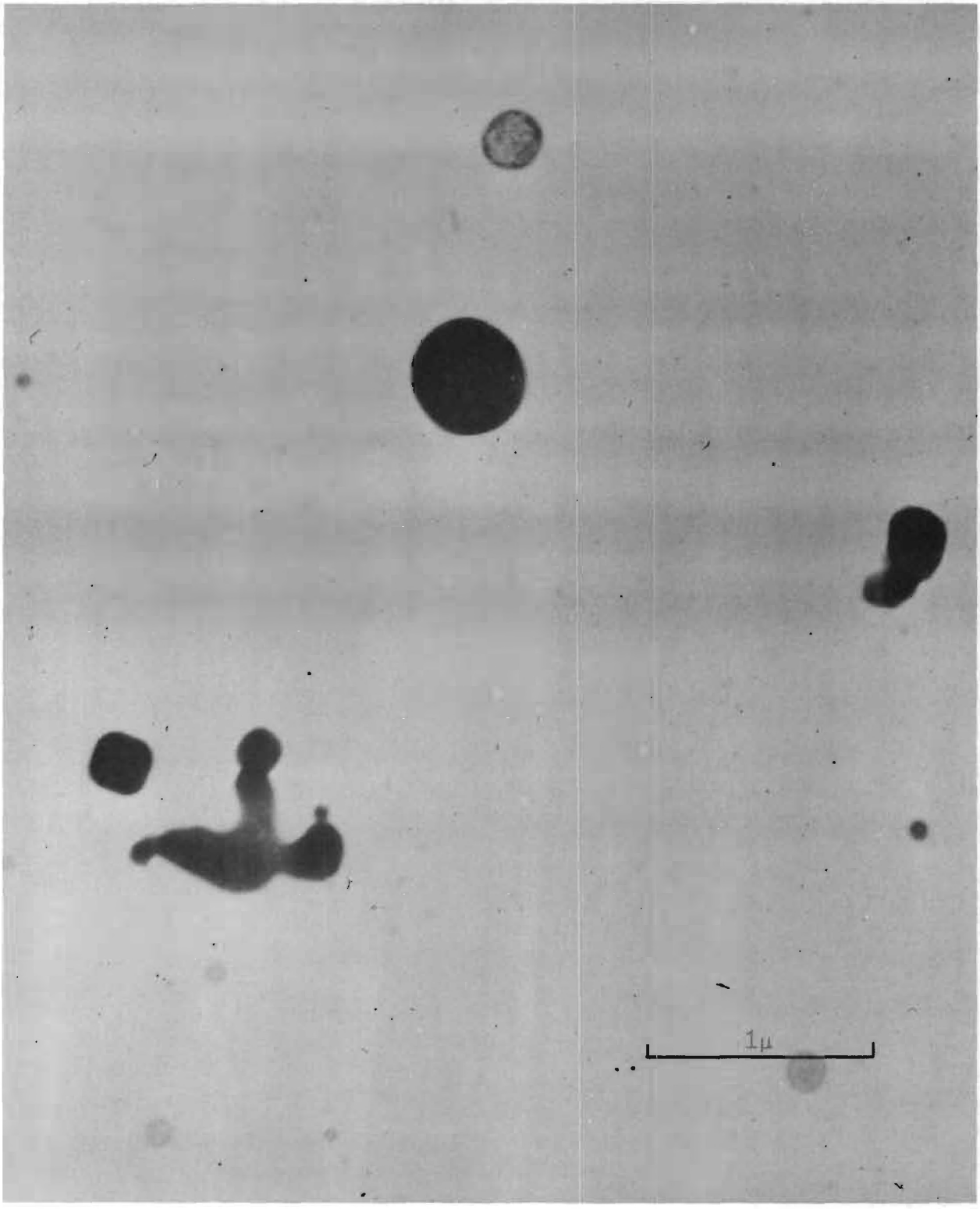

Figure 20. Ammonium Chloride Particles Exposed to Air of 35 Per Cent Relative Humidity.

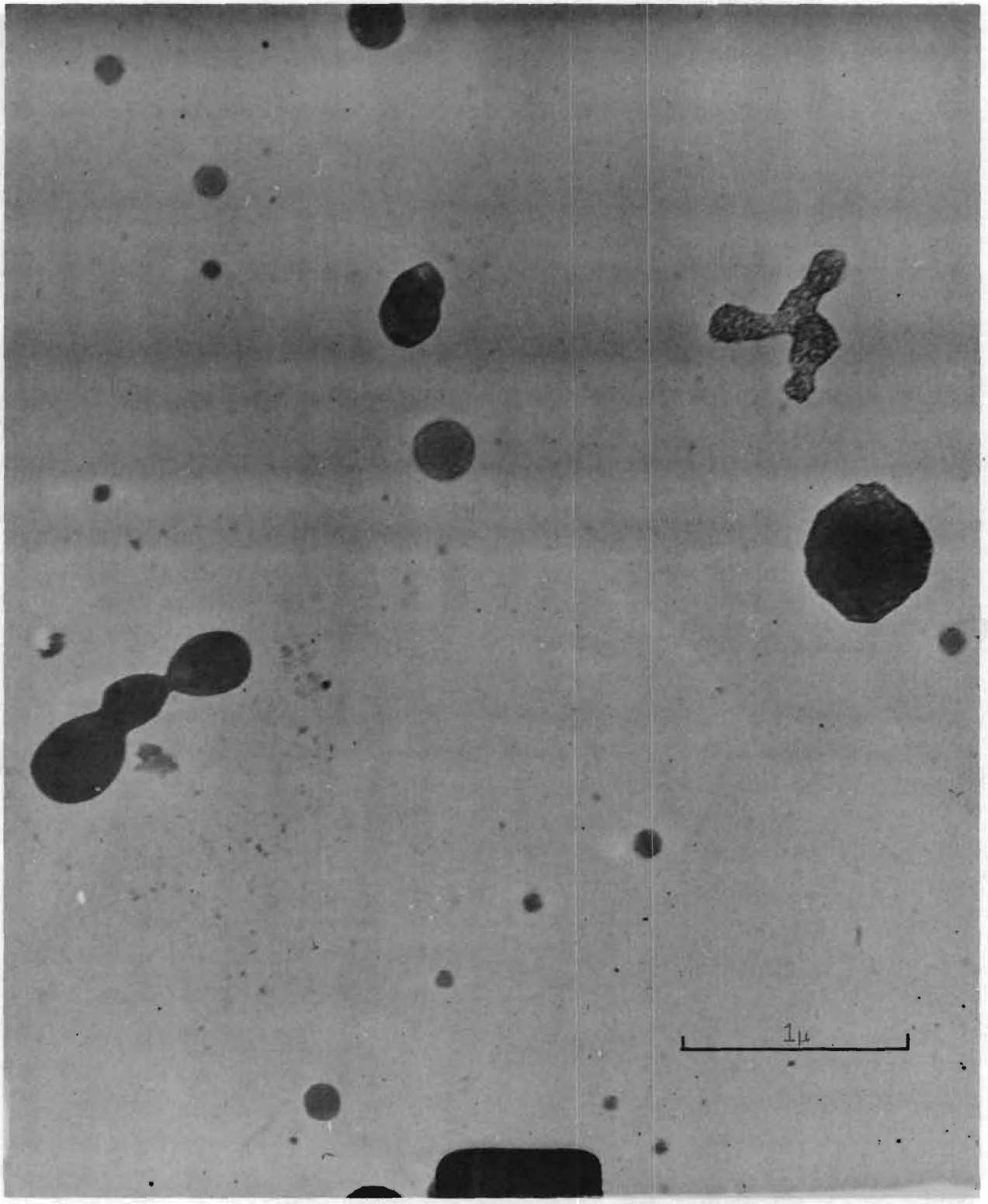

Figure 21. Ammonium Chloride Particles Exposed to Air of 40 Per Cent Relative Humidity.

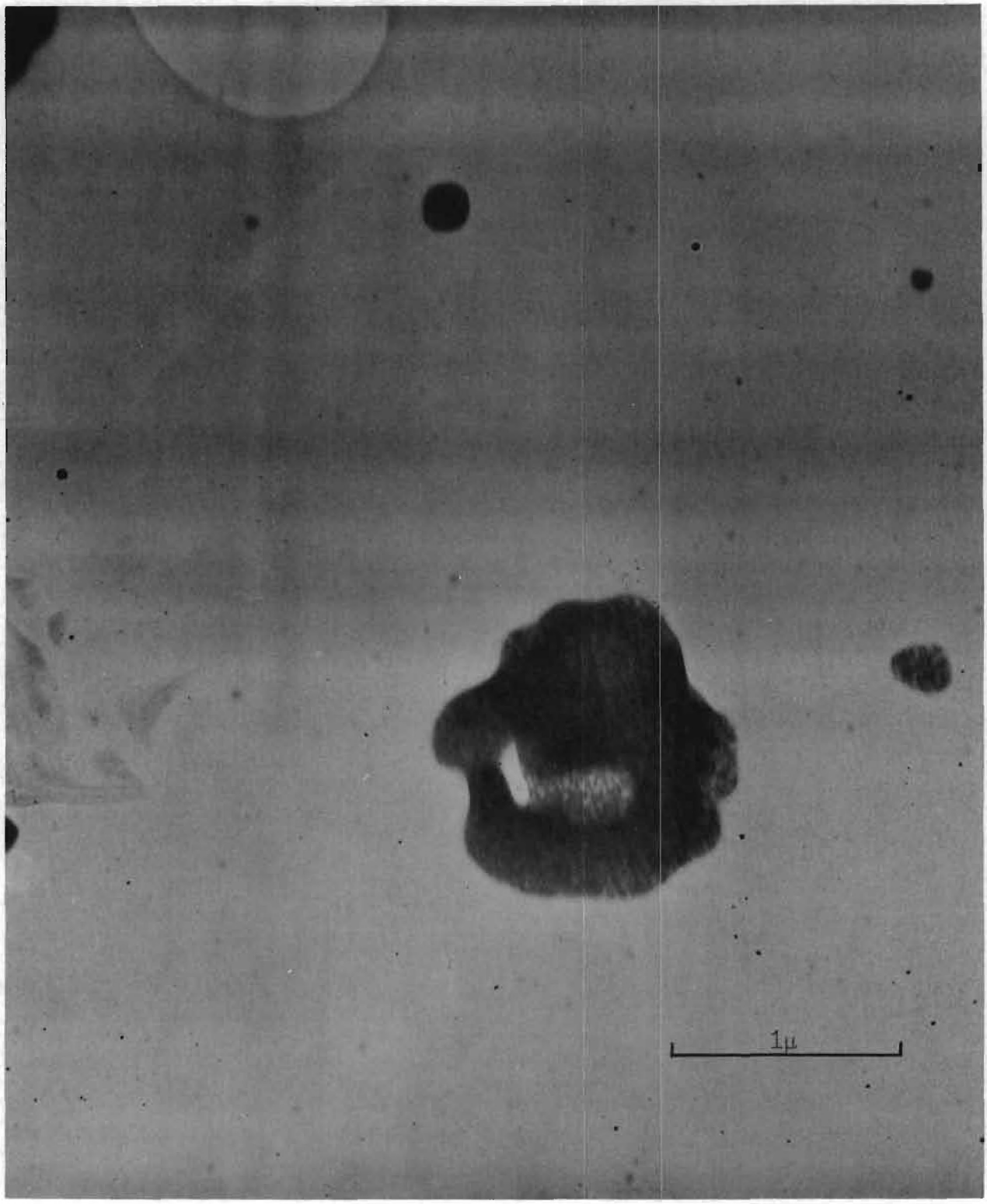

Figure 23. Ammonium Chloride Particles Exposed to Air of 50 Per Cent Relative Humidity.

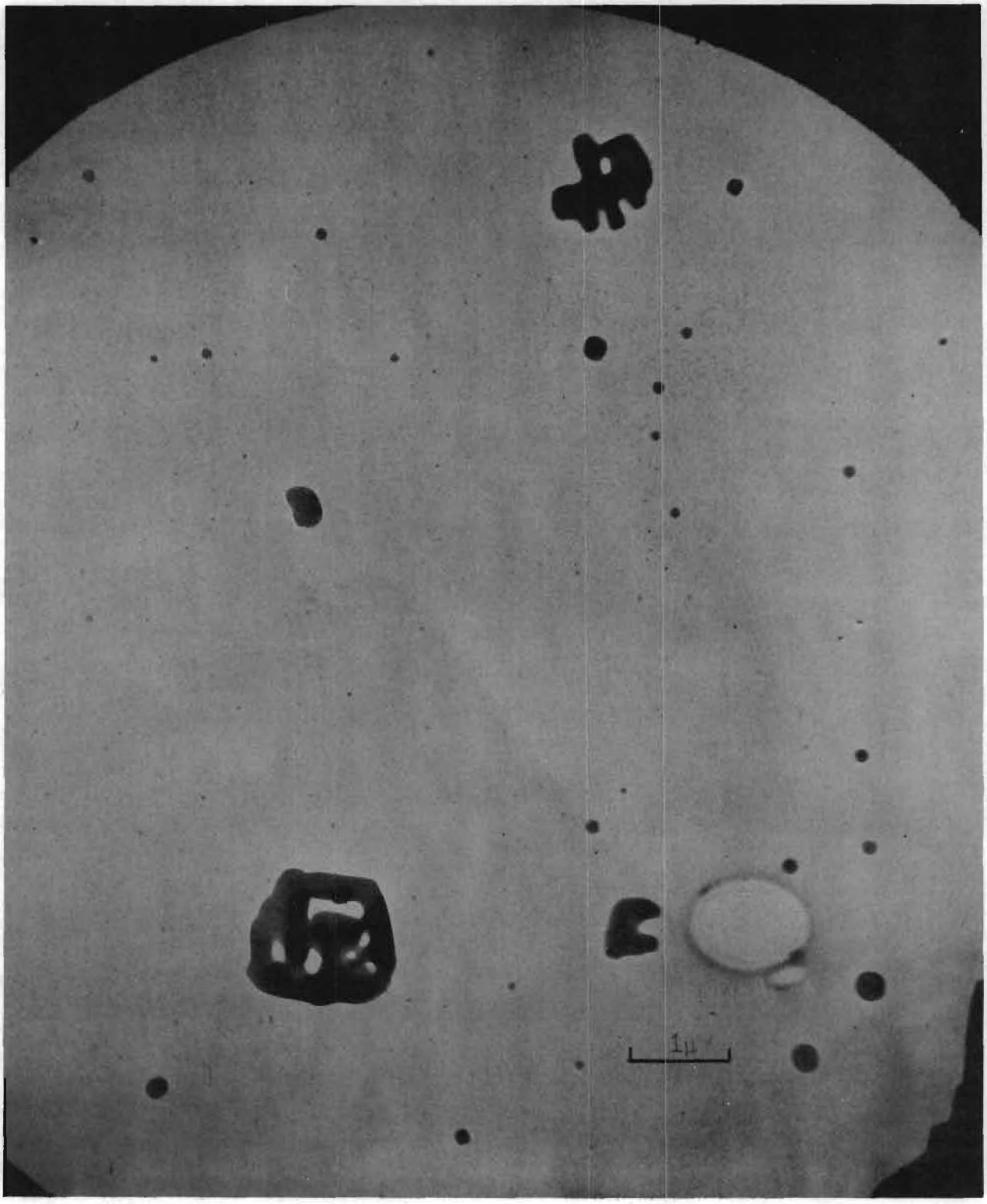

Figure 24. Ammonium Chloride Particles Exposed to Air of 50 Per Cent Relative Humidity.

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A Comparison of Methods for Fitting Bimodal Particle Size Distribution Curves

By

J. M. DALLAVALLE,
CLYDE ORR, JR., and H. G. BLOCKER

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A COMPARISON OF METHODS FOR FITTING BIMODAL PARTICLE SIZE DISTRIBUTION CURVES

ABSTRACT

Many particle size distributions are bimodal in character. They occur in the blending of two or more materials having different particle size distributions, although it is not uncommon to find a single material exhibiting two peaks in its distribution curve. Such distribution curves are also found in mixtures of feldspar and quartz, often closely associated in nature. When ground, these minerals fracture differently. This report presents two types of bimodal distributions which the authors have encountered in their studies and sets forth the necessary criteria for describing such distributions in a simple manner.

Bimodal size frequency distributions are often encountered in micromeritics. Thus far, they have received little attention. With the development of interest in particle size distributions over wider and wider ranges of size, greater consideration must inevitably be given to the fitting of multimodal distributions. Some indication of their importance is available from the emulsion globule size study of Schoenholz and Kimball[1] using the electron microscope. This report discusses procedures for analyzing bimodal distributions in particular, although the procedure can be expanded to multimodal forms. There are as yet no simple parameters for characterizing differences in various

(1) Schoenholz, D. and Kimball, C. S., "The Electron Microscope Studies. Bright-drying Wax Dispersions." Soap Sanit. Chemicals 23, 131, 133, 135 (1947).

bimodal distributions other than the location of the modes and the minimal values lying between. It is hoped that this report will stimulate further interest in the subject.

The bimodal distribution to be discussed occurred in a study of aerosol coagulation phenomena. Such distributions, however, can be prepared by the simple process of compounding two distributions (normal or skewed) to obtain one curve. Before proceeding further, it should be noted that some bimodal distributions can be represented to a fair degree of approximation by a normal curve, as shown in Figure 1 of the Appendix. The equation of a normal curve is of the form

$$y = \frac{N}{\sqrt{2\pi}\,\sigma} \exp\left[-\frac{(x - A)^2}{2\sigma^2}\right], \qquad (1)$$

where y = number of particles having a stated size x,

N = number of particles measured,

A = arithmetic mean of the distribution, and

σ = standard deviation of the distribution.

Using computed values for A and σ of 2.76 and 0.36, respectively, when N = 268, this normal equation becomes

$$y = 59.4 \exp[-(x - 2.76)^2/0.26]. \qquad (2)$$

This unimodal form does not represent the data, and it is erroneous to assume that it does.

Furthermore, it is possible to overlook the existence of a bimodal distribution if the group intervals selected for plotting (or calculating) the distribution are very large. Multimodal probability distributions are not uncommon. They occur in quantum theory in connection with the distribution of electrons about the nucleus of an atom.[2] The

(2) Pauling, L. C. and Wilson, E. B., Introduction to Quantum Mechanics, Chapter V. McGraw-Hill Book Co., Inc., New York, N. Y., 1935.

bimodal form was recognized as a possibility in statistical distribution by Kapteyn[3] and later by Fagerholt.[4] Fagerholt's general equation is rather difficult to deal with and is based on Kapteyn's theory of "reaction functions" as the causative factor in determining distribution types.

Karl Pearson's[5] important contributions to the analysis of skew distributions in terms of normal curves could undoubtedly be applied to the analysis of bimodal distributions. However, for a single skew distribution, five moments must be computed and there is involved, as well, the solution for the roots of an equation of the ninth order, a time-consuming task.

THEORY

Three methods for obtaining the fit of a bimodal distribution will be discussed. All of them will be based on the general equation

$$y = \exp[-(a_4x^4 + a_3x^3 + a_2x^2 + a_1x + a_0)] \quad , \tag{3}$$

which can be shown to represent (under certain conditions) a bimodal distribution. For simplicity, g(x) will be written for the exponential polynomial, or

$$g(x) = a_4x^4 + a_3x^3 + a_2x^2 + a_1x + a_0 \quad . \tag{4}$$

Equation (3) then takes the form

$$-\ln y = g(x) \quad . \tag{5}$$

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(3) Kapteyn, J. C., "Skew Frequency Curves (First Paper)." Groningen (1903).

(4) Fagerholt, G., "Particle Size Distribution of Products Ground in Tube Mill." Ph. D. Thesis, Den Polytekniske Laereanstalt, Denmark (1944).

(5) Pearson, Karl, "III. Contributions to the Mathematical Theory of Evolution." Phil. Trans. Roy. Soc., Ser. A. 185, Pt. I, 71-110 (1894).

The general polynomial of the fourth degree can be reduced by methods outlined in texts on advanced algebra. Thus, by multiplying and dividing through by $a^2 = a_4$,

$$g(x) = a^2(x^4 + a_3'x^3 + a_2'x^2 + a_1'x + a_0') \quad , \tag{6}$$

where $a_3' = a_3/a^2$, $a_2' = a_2/a^2$, $a_1' = a_1/a^2$, and $a_0' = a_0/a^2$. If x is replaced by $x - a_3'/4$, after reduction Equation (6) becomes

$$g(x) = a^2(x^4 + px^2 + qx + r) \quad , \tag{7}$$

where p , q , and r are new constants. Hence Equation (3) becomes

$$y = \exp[-a^2r] \cdot \exp[-a^2(x^4 + px^2 + qx)]$$

or

$$y = k \exp[-a^2(x^4 + px^2 + qx)] \quad , \tag{8}$$

where k is written for $\exp[-a^2r]$.

Equation (8) will be used to discuss the moment method of curve fitting of O'Toole.[6,7] The method of least squares and the related five-ordinate method will utilize the form of Equation (3).

Differentiating Equation (8) and setting the result equal to zero, the cubic equation

$$4x^3 + 2px + q = 0 \tag{9}$$

is obtained. The condition necessary for this equation to have three real and distinct roots is that

$$-8p^3 > 27q^2 \quad , \tag{10}$$

and this requires that $p < 0$. If $-8p^3 = 27q^2$, then two roots are equal and one of the modes coincides with the minimum; if $p = q = 0$,

(6) O'Toole, A. L., "On the System of Curves for Which the Method of Moments Is the Best Method of Fitting." Annals of Math. Statistics 4, 1-29 (1933).

(7) O'Toole, A. L., "A Method of Determining the Constants in the Bimodal Fourth Degree Exponential Function." Annals of Math. Statistics 4, 78-93 (1933).

both modes coincide with the minimum point. With respect to the peaks the following should be noted:

(a) If q is positive, the peak to the left is smaller than the one to the right, and conversely, if q is negative, the peak on the right is smaller.

(b) If the distribution is bimodal, p in Equation (8) must be less than 0, i.e., negative.

(c) If $q = 0$, the curve is symmetrical with respect to the ordinate at the minimum point.

The points of inflection can be derived from Equation (8) by taking the second derivative and setting it equal to zero. However, this is of little practical importance. For a bimodal distribution, conformity with Expression (10) is sufficient.

There is no simple solution for the area under the curve represented by Equations (3) and (8). Since a solution in infinite series would be obtained, it is preferable to use graphical methods. Thus, the constant, k, in Equation (8) is easily evaluated, for if N is the total frequency,

$$k\int_{-\infty}^{\infty} \exp[-g_1(x)]dx = N \quad , \tag{11}$$

where

$$g_1(x) = a^2(x^4 + px^2 + qx) \quad .$$

METHOD OF MOMENTS

The application of moments to fitting bimodal distributions was developed by O'Toole.[6] The reader is referred to the original investigation by O'Toole for details. Only an outline of the necessary formulas for obtaining the constants of $g(x)$ in Equations (7) and (8) will be given here.

The nth moment is defined as

$$\nu_n = \Sigma x^n f(x)/\Sigma f(x) \quad , \tag{12}$$

where x = particle diameter, and

$f(x)$ = the frequency corresponding to x.

The constants p , q , and a^2 in terms of the first six and of the eighth moments are

$$p = \frac{-B \pm \sqrt{B^2 - 10AC}}{5A} \quad , \tag{13}$$

where $A = 2\nu_4 - 6\nu_2 + 15\nu_1^2\nu_2 - 6\nu_1^4 - 5\nu_1\nu_3$,

$$B = 90\nu_1\nu_2\nu_3 - 60\nu_1^3\nu_3 - 25\nu_3^2 + 16\nu_6 - 60\nu_2\nu_4 - 21\nu_1\nu_5 + 60\nu_1^2\nu_4 \quad ,$$

$$C = 30\nu_2\nu_3^2 - 60\nu_1^2\nu_3^2 - 42\nu_3\nu_5 + 120\nu_1\nu_3\nu_4 + 12\nu_8 - 60\nu_4^2 \quad ,$$

$$q = -4\nu_3 - 2p\nu_1 \quad , \tag{14}$$

and

$$a^2 = (4\nu_4 + 2p\nu_2 + q\nu_1)^{-1} \quad . \tag{15}$$

The value of k is derived from the equation

$$k = N/\Sigma\exp[-g_1(x)] \quad , \tag{16}$$

where $\Sigma\exp[-g_1(x)]$ is made up of the calculated values (for stated intervals as in Table I below) of a^2 , p, and q.

Using the method outlined above for computing the constants a^2, p, q, and k, Equation (8) may be evaluated for the data given in Table I. These data are represented by the double-humped distribution shown in Figure 1.

TABLE I

PARTICLE SIZE FREQUENCY DISTRIBUTION HAVING A BIMODAL CHARACTER

Particle Diameter, x (microns)	Frequency y = f(x)	Particle Diameter, x (microns)	Frequency y = f(x)
0.60	1	2.40	26
0.80	2	2.60	47
1.00	4	2.80	57
1.20	4	3.00	50
1.40	3	3.20	35
1.60	1	3.40	18
1.80	1	3.60	7
2.00	2	3.80	2
2.20	7	4.00	1

From these data the following moments are obtained:

$\nu_1 = 2.769$, $\nu_5 = 212.176$,

$\nu_2 = 7.953$, $\nu_6 = 653.582$,

$\nu_3 = 23.367$, ν_7 (not needed),

$\nu_4 = 69.873$, $\nu_8 = 6458.883$.

Whence, from Equations (13), (14), and (15), values of

$$p = 1.709 \text{ or } -1.488 ,$$

$$q = -85.227 , \text{ and}$$

$$a^2 = 0.0504$$

are obtained. The negative value of p is selected in conformity with the requirement stated in Expression (10). Then from Equation (16)

$$k = 0.0034 .$$

Using the constants in the preceding paragraph, the equation

$$y = 0.0034 \exp[-0.0504x^4 + 0.0750x^2 + 4.295x] \qquad (17)$$

is found for the data of Table I. This equation is shown plotted in Figure 2. The curve is unimodal and skewed to the left. This is due to the fact that Equation (9) has only one real root. The relatively

high moments used in fitting the curve have suppressed the smaller hump to the left of the plotted data shown in the figure. On the whole, the fit is good; however, O'Toole did not obtain good results by this method when applied to a bimodal distribution having two sharply defined peaks.

METHOD OF LEAST SQUARES

The data of Table I can be fitted by least squares, using a form of Equation (3). In addition to requiring the first eight powers of the variate x, products of the form $x^n \cdot \ln y$ are also required. Five simultaneous equations are needed for obtaining a least square fit. These equations are:

$$\begin{aligned}
-\Sigma \ln y &= a_0 n + a_1 \Sigma x + a_2 \Sigma x^2 + a_3 \Sigma x^3 + a_4 \Sigma x^4 \\
-\Sigma x \ln y &= a_0 \Sigma x + a_1 \Sigma x^2 + a_2 \Sigma x^3 + a_3 \Sigma x^4 + a_4 \Sigma x^5 \\
&\vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \qquad \vdots \\
-\Sigma x^4 \ln y &= a_0 \Sigma x^4 + a_1 \Sigma x^5 + a_2 \Sigma x^6 + a_3 \Sigma x^7 + a_4 \Sigma x^8
\end{aligned} \quad , \qquad (18)$$

where n is the number of items in Table I. From the solution of these equations for a_0, a_1, a_2, a_3, and a_4, the following equation of the form of Equation (3) is obtained:

$$y = \exp[-(0.324x^4 - 2.018x^3 + 3.522x^2 - 2.367x - 0.0036)] \quad ,$$

or

$$y = 1.004 \exp[-0.324(x^4 - 6.228x^3 + 10.870x^2 - 7.306x)] \quad . \qquad (19)$$

A plot of this equation, shown in Figure 3, yields a small mode to the left which fails to coincide with that of the original data. It is difficult to explain the difference between values computed by means of Equation (19) and the observed values.

FIVE-ORDINATE METHOD

This method is based on the selection of five values of x and their corresponding values of y and solving five simultaneous equations. By selecting the values of x on either side of the modes near the top and using a fifth at the minimum point, a curve is obtained, the modes and minimum point of which coincide with the experimental data. The use of equally spaced values of x, although simplifying the computations, does not give as good a fit. Curves, obtained for different sets of coordinates, are given in Figure 4. Their equations are:

$$y = \exp[-4.2279x^4 + 32.4793x^3 - 86.1532x^2 + 92.8902x - 33.3785] \quad (20)$$

and

$$y = \exp[-0.9874x^4 + 6.7147x^3 - 14.1144x^2 + 10.1638x + 0.4684] \; . \quad (21)$$

Both equations produce bimodal distributions, but Equation (20) shows better agreement with the data.

It can be shown from an analysis of Equation (8) that a four- or five-ordinate method can be applied to a size distribution of the form shown in Figure 5. The data for the experimental curve in this figure are given in Table II. The left-hand portion of this curve rises steeply; a very rapid drop to the origin from a maximum occurs, but is not indicated in the figure. Such distributions are not uncommon in the study of emulsions. This curve was fitted by the same method as above and by using four selected ordinates. The equation representing the latter form of distribution is

$$y = \exp[-(a_3x^3 + a_2x^2 + a_1x + a_0)] \; . \quad (22)$$

Two equations calculated from sets of selected ordinates are

$$y = \exp[-1.5330x^3 + 10.1729x^2 - 18.8139x + 10.6012] \; , \quad (23)$$

and

$$y = \exp[-1.8750x^4 + 11.9951x^3 - 23.0903x^2 + 12.7290x + 2.0332] . \quad (24)$$

These equations are plotted in Figure 5.

TABLE II

PARTICLE SIZE FREQUENCY DISTRIBUTION HAVING
A BIMODAL CHARACTER

Particle Diameter, x (microns)	Frequency y = f(x)	Particle Diameter, x (microns)	Frequency y = f(x)
0.40	74	2.20	5
0.60	12	2.40	12
0.80	4	2.60	24
1.00	2	2.80	28
1.20	1	3.00	25
1.40	1	3.20	18
1.60	0	3.40	10
1.80	1	3.60	4
2.00	1	3.80	1

CONCLUSION

We may infer from the foregoing that the selected ordinate methods can give as good a fit for a bimodal distribution as the more complicated methods of moments and least squares.

Respectfully submitted,

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APPENDIX

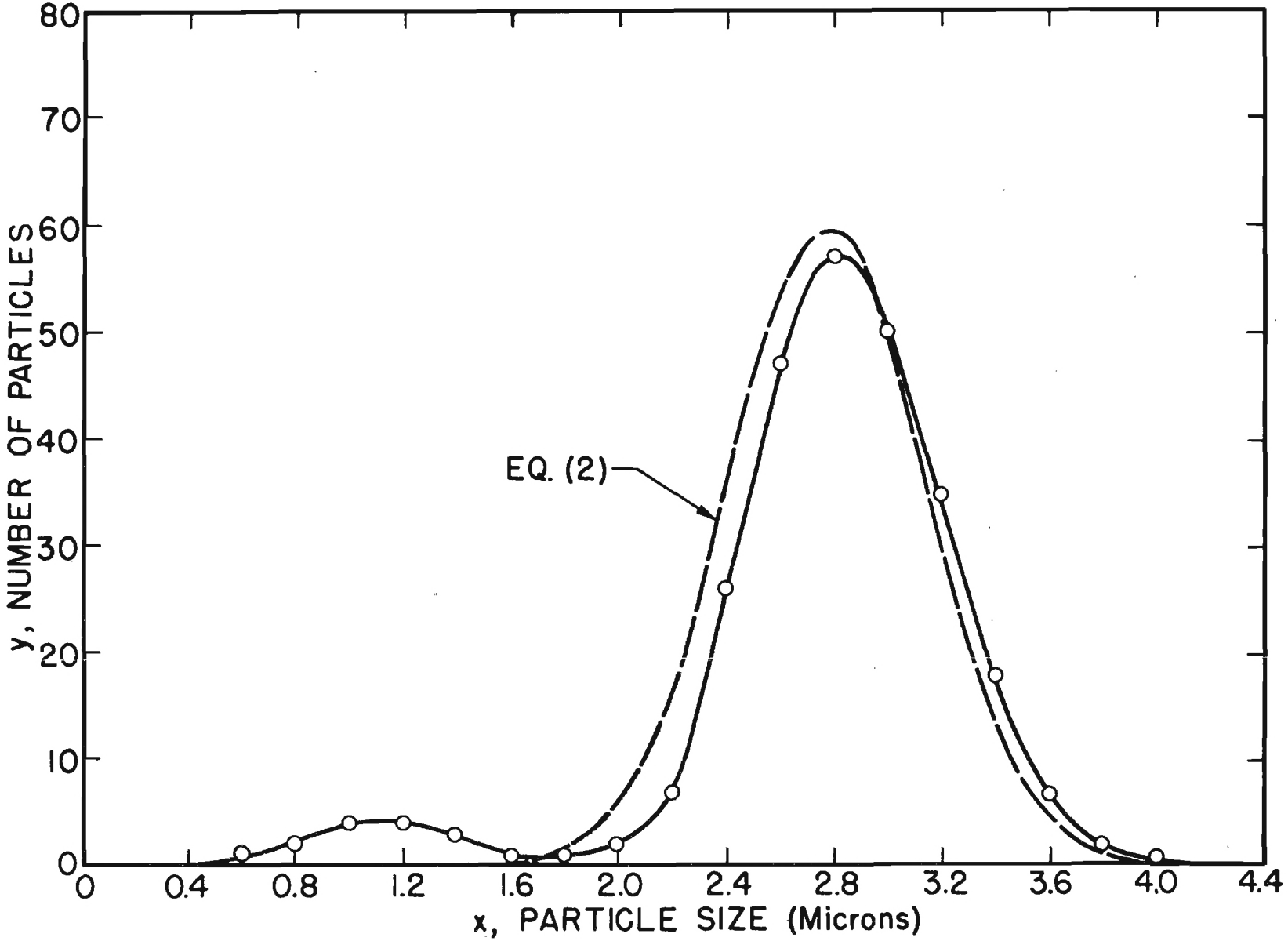

Figure 1. Bimodal Particle Size Distribution Curve Fitted by Normal Curve.

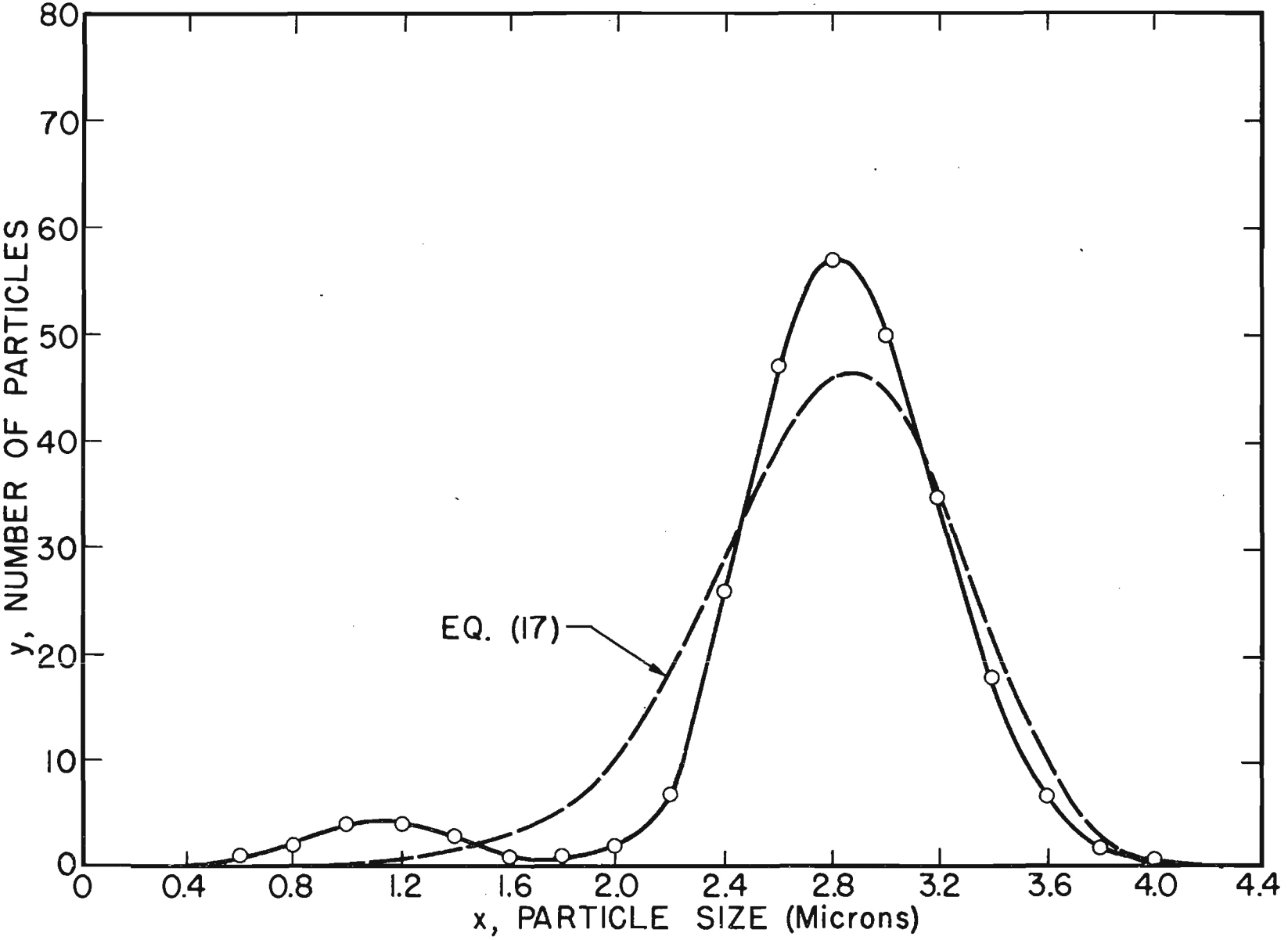

Figure 2. Bimodal Particle Size Distribution Curve Fitted by Method of Moments.

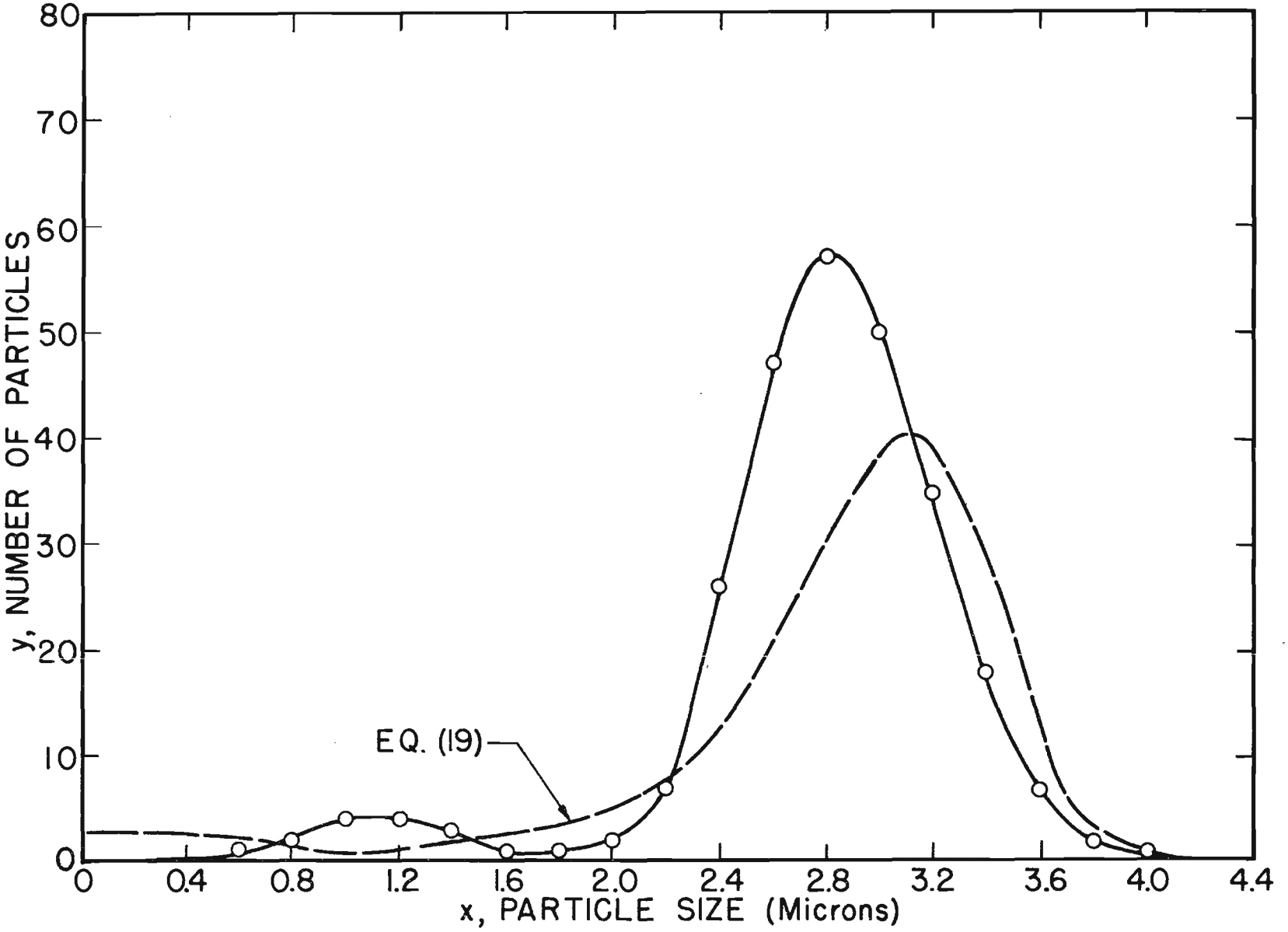

Figure 3. Bimodal Particle Size Distribution Curve Fitted by Method of Least Squares.

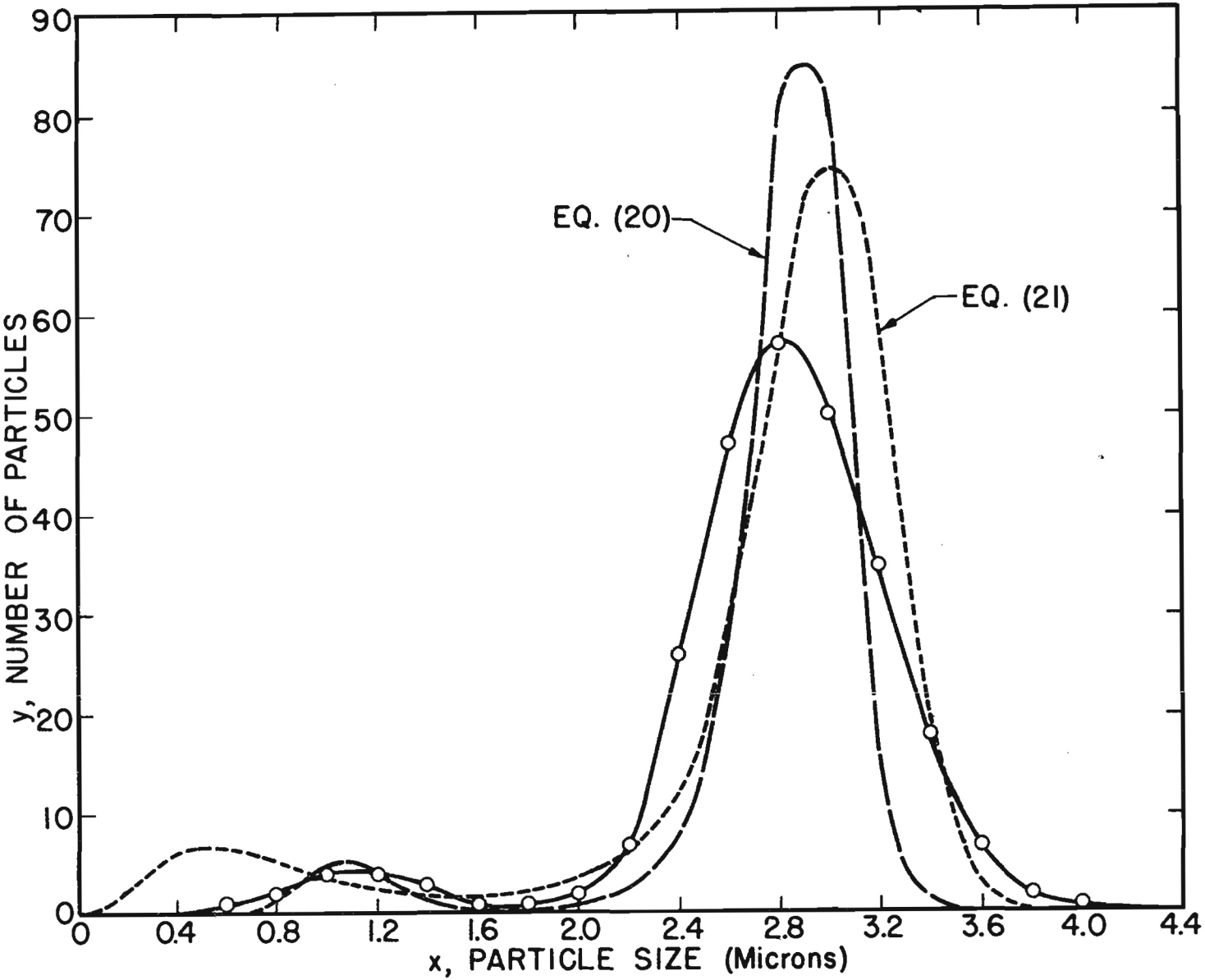

Figure 4. Bimodal Particle Size Distribution Curve Fitted by Five-Ordinate Method.

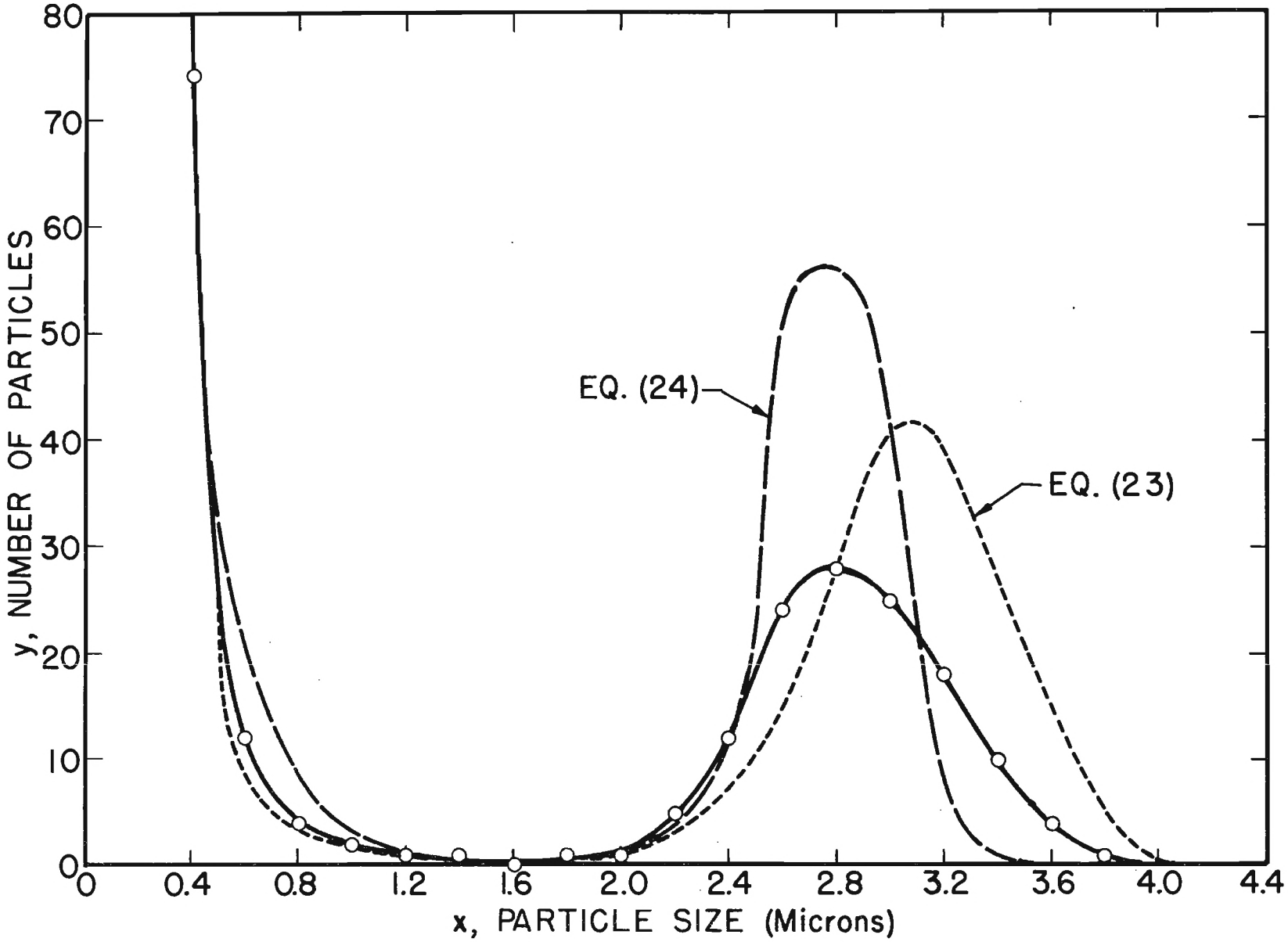

Figure 5. Bimodal Particle Size Distribution Curve Fitted by Four- and Five-Ordinate Methods.